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CHEMICAL VAPOR DEPOSITION OF CHROMIUM ON ThO_2

by

Neil D. Veigel, J. L. McCall, K. E. Meiners,
and J. M. Blocher, Jr.

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FINAL REPORT

on

CHEMICAL VAPOR DEPOSITION OF CHROMIUM ON ThO_2

(Contract No. NAS3-10492)

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Cleveland, Ohio 44135

by

Neil D. Veigel, J. L. McCall, K. E. Meiners, and J. M. Blocher, Jr.
Vapor Deposition
Optical and Electron Microscopy
and
Materials Development Divisions

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ABSTRACT

A process was developed to prepare small (5 to 16-gram) quantities of high-purity chromium-ThO_2 powder by deposition of chromium on and/or in the presence of entrained particles of ThO_2. To obtain high-purity chromium, the hydrogen reduction of CrI_2 was used as the coating reaction. On consolidation of the vapor-formed product by hot isostatic pressing, a fair dispersion of ThO_2 was obtained which appears to be stable at 2600 F (1700 K) for 100 hours, as evidenced by the fact that coalescence was limited to local modification of the ThO_2 agglomerates present in the as-pressed condition. Migration of individual ThO_2 particles or

agglomerates did not occur. However, both agglomerates and individual particles were spheroidized on heat treatment at 2600 F (1700 K).

SUMMARY

A process was developed for the deposition of chromium on and/or in the presence of entrained ThO_2 particles by hydrogen reduction of CrI_2. The process development included design and construction of laboratory-scale apparatus for (1) continuous feeding of a controlled amount of ThO_2 particles to a coating chamber, (2) continuous feeding of a controlled amount of CrI_2 to the coating chamber, (3) effective reduction of CrI_2 with hydrogen in the presence of entrained ThO_2, and (4) collection of the powder product.

The process was developed to the extent that small amounts (5 to 16 g/batch) (5×10^{-3} to 16×10^{-3} kg/batch) of chromium-ThO_2 powder were obtained of high purity with respect to the contaminants carbon ($<$20 ppm), nitrogen ($<$20 ppm), sulfur ($\approx$100 ppm), metallics ($<$450 ppm). Analyses of nonthoriated chromium indicated an oxygen content of $\approx<$1145 but $>$320 ppm. Analyses of powder samples indicated that a ThO_2 content could be obtained within about 0.5 wt % of the desired composition. Metallographic examination of the vapor-formed chromium-ThO_2 powder did not establish that the thoria was coated in the sense that individual thoria particles were completely surrounded by chromium. However, the consolidated chromium-ThO_2 contained a reasonably good dispersion with interparticle spacing in the range of 3.0 to 5.1 microns (3.0×10^{-6} to 5.1×10^{-6} m) at the ThO_2 concentrations investigated, i.e., 2, 3, and 5 vol %.

Metallographic examination of specimens heat treated at 2400 F (1590 K) and 2600 F (1700 K) for 100 hours indicated that individual ThO_2 particles and clumps of ThO_2 particles present in the as-consolidated material became spheroidized during the heat treatment. However, migration of individual particles was either minimal or did not occur.

The maximum size of ThO_2 particles in the consolidated material was larger (1.5 μ) ($1x10^{-6}$m) than the desired 0.1 micron ($1.0x10^{-7}$m). The origin of the larger size ThO_2 particle can be at least partially accounted for by the fact that the thoria powder, used as feed material for the process, contained particles ranging in size from 0.002 to 1.5 microns ($2x10^{-9}$ to $1.5x10^{-6}$m). Although it is possible that some agglomeration of smaller particles occurred during the vapor-forming process and/or during consolidation, some improvement in the material that has already shown promise with respect to stability at 2600 F (1700 K) can be expected if a better quality ThO_2 feed material can be obtained.

INTRODUCTION

Dispersion-strengthened chromium is of interest for use in turbines which require materials having high-temperature strength and oxidation resistance. To be effective at elevated temperatures, the dispersoid must be stable in contact with the matrix and impurities associated with the matrix.

Thoria was believed to be a promising material for the dispersion-strengthening of chromium. However, the task of preparing a good dispersion of ThO_2 in a pure chromium matrix is a formidable one. Methods for the preparation of high-purity chromium alone in either powder or massive form are not abundant.

Fused-salt electrolysis, hydrogen treatment of electrolytic chromium, and a modified Van Arkel-de Boer iodide process have been used to prepare massive chromium deposits of respectable purity (99.90 wt % Cr or better). However, none of these are readily adaptable for incorporation of submicron-size ThO_2 in the chromium. Reduction of the massive chromium by grinding to submicron size to permit adequate blending with ThO_2 may result in substantial contamination of the chromium powder. The normal grain growth characteristics of chromium deposited by either the thermal decomposition or hydrogen reduction of chromium halides are such that oxides are rejected by the growing crystals. Thus, the incorporation of a dispersed oxide is made difficult. Application of pure chromium coatings on submicron ThO_2 appears to be an attractive alternative. However, here again suitable methods for preparation have not been available. Deposition of pure chromium on fluidized oxide particles of several microns in size is difficult at best as a result of agglomeration, while deposition on single submicron-size particles is almost impossible. Instead of coating individual particles, agglomerates of oxide particles are formed and coated. With this information in mind, it was proposed to develop a process to coat submicron ThO_2 carried by entrainment through a coating apparatus. The obvious advantages of this approach are (1) a means of deagglomerating the submicron ThO_2 can be built into the ThO_2-feed system, (2) agglomeration on coating can be minimized by limiting particle-to-particle contact, and (3) a mixture of submicron chromium and ThO_2 powder may be obtained as either the primary or as a secondary product which can yield an adequately blended product, even if nucleation of chromium on ThO_2 does not occur to the extent that would characterize a particle coating.

Thus, Battelle-Columbus Laboratories undertook the investigation of the chemical vapor deposition of chromium on entrained thoria particles. The primary objective was to demonstrate the feasibility of the process for preparation of the chromium-ThO_2 powder which, on consolidation by hot isostatic pressing, would be stable at 2600 F (1700 K) for 100 hours. The target characteristics for the dispersion were:

(1) Volume percentage of dispersoid: Up to 5 vol % ThO_2.

(2) Dispersoid particle size: Up to 0.1 micron (1×10^{-7}m) with 50 percent less than 0.05 micron (5×10^{-8}m).

(3) Interparticle spacing: Up to 1.5 microns (1.5×10^{-6}m).

(4) Impurities: Less than 50 ppm of nitrogen and carbon, with no other impurity greater than 100 ppm.

The coating process believed to be most suitable for the preparation of the chromium-ThO_2 dispersion involves a controlled continuous feed of the individual thoria particles into a stream of hydrogen, and transport of the particles by entrainment into a heated reduction tube.

Concurrently, solid particles of CrI_2 are metered continuously to an evaporator. On vaporization, the CrI_2 is carried with helium into the reaction zone where the CrI_2, hydrogen, and entrained ThO_2 are brought into contact. Deposition of chromium on the ThO_2 and/or formation of chromium powder results from hydrogen reduction of the CrI_2. The product is then disentrained downstream from the reduction chamber and collected for consolidation by hot isostatic pressing.

PREPARATION OF CHROMIUM-ThO_2 POWDER

General Discussion

A total of 24 separate preparations were concluded in this investigation. The conditions and results of the preparations are summarized in Table 1. Since the objective of the investigation was to determine the feasibility of the preparation of a dispersion-strengthened chromium, a systematic study of process parameters was not undertaken. Instead, the conditions used were not altered appreciably from those known to yield a useful product. Substantial modifications of apparatus were also limited for the same reason. The first 10 preparation runs were made to check out procedures while the latter runs, except Run No. 24991-48-14, were specifically intended for the preparation of material for evaluation.

In general, it is known from previous experience and from thermodynamic data that efficiency of chromium formation by hydrogen reduction of CrI_2 increases with temperature and hydrogen concentration. Consequently, the highest temperature compatible with the materials of construction (Vycor and quartz), and the highest hydrogen feed rate compatible with other components of the system were used.

TABLE 1. SUMMARY OF DATA ON PREPARATION OF CHROMIUM-ThO_2 POWDER

Run No.	Coating Temp F	Coating Temp K	Hydrogen Concn, mole %	CrI_2 Concn, mole %	Gas Flow Pattern(1)	Overall Conversion Eff, %(2,3)	ThO_2 Feed Rate g/hr	ThO_2 Feed Rate Kg/Sx10[7]	Description and Location of Chromium: Fraction of Product as Coating on Reactor, %	Fraction of Product as Powder Deposited in Exhaust Section of Coating Reactor, %	Fraction of Product as Powder Collected in Product Flask, %	Chromium-ThO_2 Powder Preparation Rate: Total Powder Formed g/hr	Total Powder Formed Kg/Sx10[7]	Powder Collected in Product Flask g/hr	Powder Collected in Product Flask Kg/Sx10[7]	ThO_2 Content, vol %
24991-15-1	1830	1270	52.4	0.84	A	55-76	≈1	≈2.78	62.2	26.6	11.2	2.9	8.0	-	-	-
24991-17-2	Ditto		61.1	0.68	Ditto		Ditto	Ditto								-
24991-20-3	"		49.7	0.52	"	56-74	"	"	66.4	19.8	13.8	3.1	8.6	-	-	-
24991-21-4	"		66.2	0.70	"		"	"								-
24991-23-5	"		None	0.95	B	11.1	None	None	100	None	None	None	None	None	None	None
24991-24-6	"		37.2	0.90	C	51-71	≈1	≈2.78	35.8	33.8	30.4	7.4	20.6	3.6	10.0	-
24991-26-7	"		60.6	0.56	Ditto	53-83	Ditto	Ditto	21.7	42.1	36.2	9.4	26.1	5.1	14.2	-
24991-28-8	"		79.6	0.53	"	63-92	-	-	52.4	26.0	21.6	6.1	16.9	2.8	7.8	3.0
24991-31-9	1900	1310	79.8	0.51	D	81-86	1.45	4.02	44.3	15.7	40.0	8.9	24.7	4.4	12.2	10.0
24991-33-10	Ditto		79.6	0.47	Ditto	77-90	0.22	0.61	50.4	18.0	31.6	6.6	18.3	4.0	11.1	1.6
24991-38-11	"		Ditto	0.52	"	81-92	0.47	1.31	43.1	30.5	26.4	8.7	24.2	Ditto	Ditto	2.0
24991-41-12	"		"	0.57	"	75-82	1.21	3.36	42.4	22.4	35.2	9.3	25.8	5.7	15.8	5.0
24991-44-13	1850	1280	"	0.56	"	85-95	0.71	1.97	44.4	26.9	28.7	9.7	27.0	5.0	13.9	3.3
24991-48-14	Ditto		78.9	0.39	"	74-92	None	None	45.8	18.6	35.6	5.2	14.5	3.4	9.4	None
24991-50-15	1900	1310	79.7	0.49	"	78-94	0.56	1.56	57.8	16.9	25.3	5.9	16.4	3.5	9.7	3.3
24991-52-16	Ditto		Ditto	0.58	"	86-92	Ditto	Ditto	60.4	19.2	20.4	7.1	19.7	3.7	10.3	2.9
24991-54-17	"		"	0.54	"	87-93	0.33	0.92	57.2	21.8	21.0	Ditto	Ditto	3.5	9.7	1.2
24991-57-18	1830	1270	78.0	0.53	E	77-88	0.36	1.00	41.7	23.4	34.9	8.0	22.2	4.8	13.4	0.3
24991-60-19	Ditto		79.7	0.33	F	97-99	0.32	0.89	66.7	15.4	17.9	3.9	10.8	2.1	5.8	-
24991-62-20	"		76.2	0.39	Ditto	>57 (4)	0.33	0.92	23.1	29.0	47.9	3.4	9.4	Ditto	Ditto	1.5
24991-64-21(5)	"		-	-	D	-	-	-	-	-	-	-	-	-	-	-
24991-66-22	1850	1280	79.7	0.57	Ditto	-	0.34	0.89	-	-	-	7.3	20.3	4.0	11.1	≈0.3
24991-68-23	Ditto		80.2	0.62	"	78-89	0.29	0.81	65.1	7.9	27.0	6.1	16.9	3.4	9.4	Ditto
24991-71-24	1830	1270	75.7	0.57	"	-	0.56	1.56	-	-	-	-	-	3.1	8.6	2.0

Footnotes - Table 1

(1) A - All gases, CrI_2, and ThO_2 were fed through concentric nozzles located in the top of the coating unit.

B - Helium plus ThO_2 and helium plus CrI_2 were fed from concentric nozzles in the top of the coating unit.

C - Helium plus CrI_2 was fed from a nozzle in the top of the coating unit, while hydrogen plus ThO_2 was fed from a nozzle in the bottom of the unit with opposing directions of flow.

D - Same as C, with additional hydrogen fed from the top of the coating unit along the inner circumference of the reactor wall.

E - Same as D, except a 25-mil (6.35×10^{-4}m) ID tube was substituted for the 47-mil (1.19×10^{-3}m) ID ThO_2 injector tube used in other runs.

F - Same as E, except three 25-mil (6.35×10^{-4}m) ID ThO_2 injector tubes were used.

(2) The coating unit was not dismantled after Runs Nos. 24991-15-1 and 24991-20-3. Therefore, the results reported are those of the sequences.

(3) As expected, material balances indicated some loss of CrI_2 and/or Cr by incomplete electrostatic precipitation of solids entrained in the exhaust gases. Since the composition of the material blown out is not known, the reaction efficiencies were calculated on the basis (1) that all of the material lost was CrI_2, and (2) that all of the material lost was Cr. The difference in the two efficiency numbers reported is equal to the fraction of chromium that may have been lost in the exhaust gases.

(4) Low efficiency not believed to be real. Suspect weighing error in the amount of CrI_2 fed.

(5) Heating element failed early in the run, and no data were obtained.

Interpretation of Process Data

Examination of the data of Table 1 provides the useful information listed below:

(1) Pyrolysis of CrI_2 in a helium atmosphere resulted in the deposition of dense chromium at low efficiency (11.1 percent). (See Run No. 24991-23-5.) With hydrogen present to effect reduction, deposition efficiencies up to about 90 percent were obtained.

(2) The preparation rate of chromium powder was essentially the same with or without the presence of ThO_2 particles. (Compare results of Run No. 24991-48-14 with all others, except Run No. 24991-23-5.)

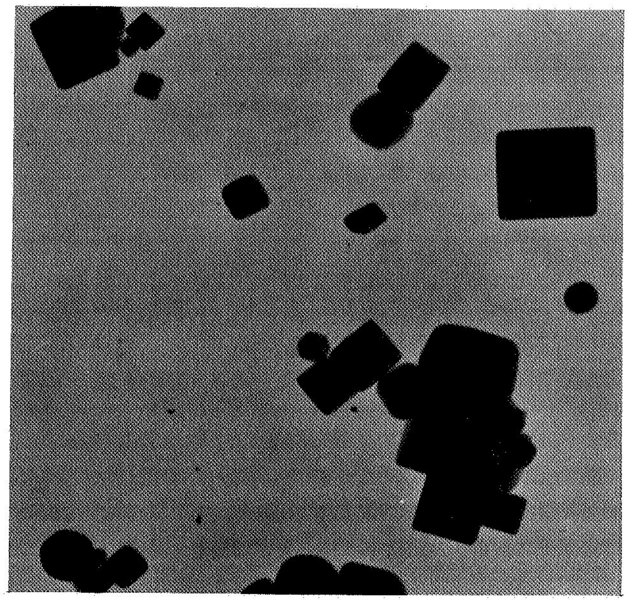
(3) Examination of the data does not indicate a detectable trend of powder-yield rate with ThO_2-feed rate.

(4) A general trend of increased efficiency with hydrogen concentration may be indicated. However, the correlation is poor, presumably as a result of the masking effects of minor changes made in the apparatus which altered the gas-flow patterns. It should also be noted that the gas-flow pattern may have changed within any single experiment as a result of deflection

of the gas by chromium deposited on the helium-CrI_2 feed nozzle.

(5) In the range of conditions investigated, there is no obvious relationship between the fraction of chromium formed as powder or as foil on the reactor wall and the conditions of temperature, hydrogen concentration, and CrI_2 concentration.

Based on the above information, it can be concluded that both homogeneous and heterogeneous nucleation of chromium occur, as evidenced by the facts that (1) entrained ThO_2 need not be present for the formation of chromium powder, and (2) a significant fraction of chromium is deposited as foil. The magnitude of the heterogeneous deposition, desired for the coating of ThO_2, should be proportional to the fraction of chromium deposited as foil. However, the lack of information on uncontrolled variations in the gas-flow pattern mask any obvious relationship. The evidence for the coexistence of both heterogeneous and homogeneous nucleation is consistent with the results obtained by metallographic examination of as-prepared chromium-ThO_2 powder. A comparison of Figures 1, 2, and 3 indicates that the chromium powder prepared without the addition of thoria consists of well-defined cubic and hexagonal particles, 200 to 4000 angstroms (2×10^{-8} to 4×10^{-7}m) in size, while the chromium-ThO_2 powder consists of less regularly shaped chromium particles of nearly the same size, with ThO_2 visible on the surface of the chromium. The irregular shape of the chromium-ThO_2 powder indicates either that the chromium nucleated on the ThO_2, or that ThO_2 came in contact and was attached to the chromium during the growth of the chromium particle. Either



30,000X 1μ EH-1034

FIGURE NO. 1. CUBIC AND HEXAGONAL CHROMIUM POWDER PREPARED WITHOUT ADDITION OF ThO_2 (Run No. 24991-48-14)

30,000X 1μ EH-989

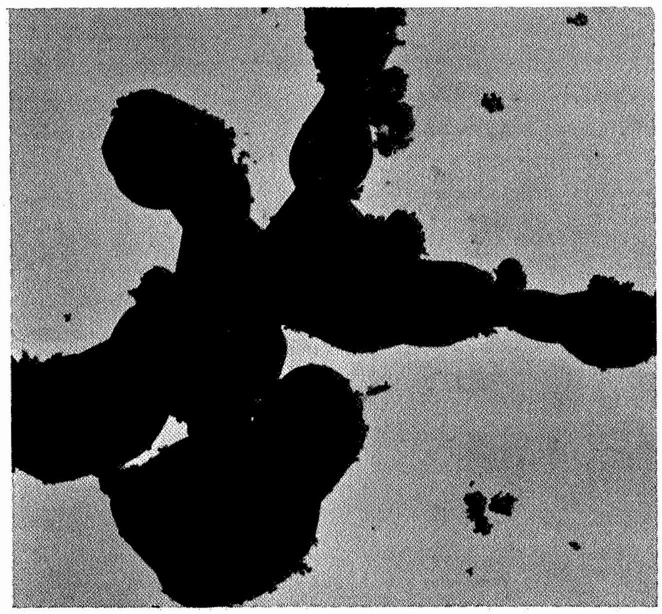
FIGURE NO. 2. ThO_2 POWDER USED FOR PREPARATION OF CHROMIUM-THORIA POWDER

15,000X 1μ EH-1029

FIGURE NO. 3. SHAPE OF CHROMIUM-ThO_2 POWDER IN THE AS-PREPARED CONDITION (Run No. 24991-41-12) situation is desirable for the preparation of a dispersion, provided that the size of the chromium particles is small. The composition of the smallest Cr-ThO_2 particles visible in Figure 3 is not known. On hydrogen heat treatment of the as-prepared powder at 1470 F (1070 K) for 4 hours to remove residual CrI_2, the chromium particles coalesce as shown in Figure 4, with ThO_2 particles visible on the surface of the chromium.

Control of ThO_2 Addition

The continuous addition of ThO_2 at rates of 0.2 to 1.5 grams per hour (5.56×10^{-8} to 4.6×10^{-7} kg/s) can be effectively controlled, as indicated by the data summarized in Table 2. The apparatus and procedure for the feeding of ThO_2 are described in detail in a later section of this report. The distribution of ThO_2 in foil and powder was determined by analysis of the chromium formed in Run No. 24991-41-12 in which the thoria feed was well controlled. The product powder collected in an electrostatic precipitator contained 6.67 wt % ThO_2 which is in excellent agreement with a predicted average value of 6.98 wt % calculated on the basis of feed rates. The powder retained in the reactor and not recovered for consolidation contained 11.5 wt % ThO_2, while a sample of foil from the reactor wall contained 0.5 wt % ThO_2. The low ThO_2 content of the foil was not unexpected in the light of results obtained in fluidized-bed coating experiments made previously at Battelle in an effort to incorporate ThO_2 into chromium as it formed coatings on 180-micron (1.8×10^{-4} m) diameter particles. The ThO_2 powder was rejected by the chromium in the growth process. Electron micrographic examination of another sample of the



7,500X $\underline{1\mu}$ EH-1030

FIGURE NO. 4. SHAPE OF CHROMIUM-COATED ThO_2 POWDER HYDROGEN HEAT TREATED AT 1470 F (1070 K). (Run No. 24991-38-11)

TABLE 2. SUMMARY OF DATA ON CONTROL OF ThO_2 ADDITION TO VAPOR-FORMED CHROMIUM

Run No.	Target Compositions Wt %	Target Compositions Vol %	Analyses of Chromium-ThO_2 Powder Wt %	Analyses of Chromium-ThO_2 Powder Vol %
24991-33-10	2.71	2	2.12	1.6
24991-38-11	2.71	2	2.77	2.0
24991-41-12	6.71	5	6.67	5.0
24991-44-13	4.04	3	4.37	3.3
24991-50-15	4.04	3	4.45	3.3
24991-52-16	4.04	3	3.95	2.9
24991-54-17	2.71	2	1.66	1.2
24991-57-18	2.71(1)	2(1)	0.38	0.3
24991-62-20	4.04(2)	3(2)	2.00	1.5
24991-66-22	4.04(3)	3(3)	<0.1	<0.1
24991-68-23	4.04(3)	3(3)	<0.1	<0.1
24991-71-24	4.04(3)	2.5(3)	2.69	2.0

(1) Changed ThO_2 injector from the 47-mil (1.19×10^{-3}m)-ID tube used in the previous preparations to a 25-mil (6.35×10^{-4}m)-ID tube.

(2) Same as (1), except three 25-mil (6.35×10^{-4}m)-ID tubes were used.

(3) A 47-mil (1.19×10^{-3}m)-ID tube was again used to inject the ThO_2. However, ThO_2 that had been dispersed in water and freeze-dried was used as the feed material. The feed rate of the freeze-dried product was lower than that obtained with a dry free-flowing ThO_2 powder used in previous preparations, and as a result the target compositions were not attained.

foil revealed a clean microstructure. Therefore, it is believed that the ThO_2 found by chemical analyses of the foil was lodged in surface irregularities. Fortunately, the higher ThO_2 content of the powder in the reactor appears to compensate for the lower thoria content of the foil.

Purity of Chromium-ThO_2 Powder

Analyses of representative samples of the chromium-ThO_2 powder are summarized in Table 3. The analyses indicate that high-purity chromium-ThO_2 powder can be prepared and consolidated without appreciable contamination. The target maximum compositions were achieved for N (50 ppm), C (100 ppm), S (100 ppm), and all other elements (100 ppm) with the exceptions that iron was present at 200 ppm, and oxygen probably exceeded the 100-ppm target. The magnitude of contamination with oxygen as Cr_2O_3 is uncertain because of limitations of methods for analyses in the presence of several wt % ThO_2.

In order to gain information on the oxygen contamination, chromium powder was prepared in Run No. 24991-48-14 without the addition of ThO_2. The product of the chromium preparation was cold pressed at 30,000 psi (2.07×10^8 N/m^2) in a helium-filled die into two pellets. To simulate the procedure used for most of the chromium-ThO_2 pellets, one of the pellets was sintered in hydrogen for three hours at 2370 F (1570 K). The hydrogen-sintered coupon contained 320-ppm oxygen and 9-ppm nitrogen, while the unsintered coupon contained 1145-ppm oxygen and 185-ppm nitrogen. The fact that the nitrogen was high in the unsintered pellet indicates that the pellet was contaminated in the pressed condition by exposure to air on loading into the vacuum-fusion apparatus. Therefore, it is concluded that the actual oxygen content is less

TABLE 3. SUMMARY OF ANALYSES OF CHROMIUM-ThO_2 POWDER FOR IMPURITIES, ppm

Run No.	Condition of Sample	C	N	S	Al	B	Ca	Cu	Fe	Mg	Mo	Ni	Si
24991-33-10	As-prepared powder, exposed to air	110	270	-	-	-	-	-	-	-	-	-	-
24991-38-11	Cold pressed at 30,000 psi (2.07x $10^8 N/m^2$) and hydrogen treated at 2370 F (1570 K) for 3 hours	20	20	-	10	20	10	70	200	10	10	50	50
24991-41-12	Ditto	20	10	-	10	20	40	10	200	10	10	50	100
24991-41-12	Ditto, plus pressure bonded (Pellet No. 12-1)	-	20	-	-	-	-	-	-	-	-	-	-
24991-44-13	Cold pressed at 30,000 psi (2.07x $10^8 N/m^2$) and hydrogen treated at 2370 F (1570 K) for 3 hours	10	20	-	-	-	-	-	-	-	-	-	-
24991-44-13	Ditto, plus pressure bonded (Pellet No. 13-2)	-	-	120(1)	-	-	-	-	-	-	-	-	-
24991-52-16	Cold pressed at 30,000 psi (2.07x $10^8 N/m^2$) and pressure bonded (Pellet No. 16-2)	-	70	-	-	-	-	-	-	-	-	-	-

(1) Previous experience with sulfur analyses in chromium indicate that the combustion method used gives reproducible results, but has a built-in blank. In an attempt to determine the blank, high-purity iodide chromium was analysed along with the chromium-ThO_2 powder. The method indicated that the iodide chromium contained 50-ppm sulfur, while duplicate samples of chromium-ThO_2 powder analysed 100- and 130-ppm sulfur. Consequently, it is believed that the sulfur content of the chromium-ThO_2 powder is actually <100 ppm.

than 1145-ppm O_2 and probably more than 320 ppm, assuming no pick up on handling and assuming some reduction of Cr_2O_3 in the hydrogen-sintering treatment.

It is noteworthy that only ThO_2 was identified by electron-diffraction patterns obtained on particles extracted from the cold-pressed (30,000 psi) ($2.07 \times 10^8 N/m^2$) and hydrogen-sintered (3 hours at 2370 F) (1570 K) product of Run No. 24991-33-10. Another indication that Cr_2O_3 contamination is not severe was obtained from the results of an electron-beam scan of the extracted particles from Run No. 24991-33-10 for the presence of chromium. The probe detected the presence of only a few particles containing chromium, which indicated a low level of oxygen present as Cr_2O_3.

An X-ray diffraction powder pattern, made from a carbon extraction replica on material consolidated by hot isostatic pressing (Pellet No. 12-1 from chromium-powder preparation Run No. 24991-41-12), also confirmed that the oxygen contamination was not severe. The pattern showed only ThO_2 to be present in the extracted material. The analysis was performed in an evacuated Debye-Scherrer camera with chromium radiation. Based on the sensitivity of the method, it is estimated that ThO_2 must account for more than 98 wt % of the extracted material and any other constituents, such as Cr_2O_3, would have to be present in concentrations less than 2 wt %. Based on the results of the X-ray diffraction and ThO_2 analyses for Pellet No. 12-1, the oxygen contamination as Cr_2O_3 is calculated to be less than 0.088 wt %.

ThO_2 Feed Material

To be suitable for use in the process developed for the preparation of chromium-ThO_2 powder, the ThO_2 should be dry with no chemically combined water present, it should be free flowing, and should contain no fused agglomerates. The desired particle size for the investigation was a maximum of 0.1 micron ($1x10^{-7}$m), with 50 percent of the particles less than 0.05 micron ($5x10^{-8}$m). It was understood that ThO_2 was available commercially, which was reported to have the desired characteristics with particles in the size range of 0.02 to 0.05 micron ($2x10^{-8}$ to $5x10^{-8}$m). However, electron-microscopic examination of the purchased material revealed the presence of fused agglomerates and particles ranging in size from 0.002 micron to 1.5 microns ($2.0x10^{-9}$ to $1.5x10^{-6}$m) (See Figure 2). A source of a more suitable ThO_2 was not located.

In an attempt to obtain a small quantity of ThO_2 for experimental use, an agglomerated thoria having a reported particle size of 0.005 to 0.015 microns ($5.0x10^{-9}$ to $1.5x10^{-8}$m) and supplied by NASA, was dispersed in water and freeze-dried. A free-flowing powder was obtained and used for feed in Run No. 24991-71-24. However, no significant improvement in the dispersion of ThO_2 in the consolidated product was obtained.

CONSOLIDATION OF CHROMIUM-ThO_2 BY HOT ISOSTATIC PRESSING

A total of 20 chromium-ThO_2 alloy pellets were consolidated by hot isostatic pressing (HIP). The results are summarized in Table 4.

All of the pellets were cold pressed at 30,000 psi ($2.07x10^{8}N/m^{2}$) in a 0.50-in. ($1.27x10^{-2}$m)-diameter die under a helium atmosphere. Ten of the pellets had been heat treated in hydrogen at 2370 F (1570 K) for three hours after being cold pressed, while the others were in the as-pressed condition. Those pellets that had been hydrogen sintered were handled in air without significant contamination, as evidenced by the analyses (20-ppm N) of the hot isostatically pressed Pellet No. 12-1. The pellets that had been

TABLE 4. DENSITY AND POROSITY OF HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 ALLOYS PREPARED BY CHEMICAL VAPOR DEPOSITION

Run No.	HIP Container No.(1)	Pellet No.	Condition of $Cr-ThO_2$ Powder Prior to HIP(2)	ThO_2 Content, vol %	Theoretical Density(3) g/cm^3	Theoretical Density(3) Kg/m^3	Bulk Density(4), %	Open Porosity(4) vol %
24991-38-11		11-1	A	2.00	7.26	7.26×10^3	98.7	0.4
		11-2	A	2.00	7.26	7.26×10^3	100.0	0.5
	1	12-1	A	4.98	7.34	7.34×10^3	98.5	0.5
24991-41-12		12-2	A	4.98	7.34	7.34×10^3	98.3	0.3
		12-3	A	4.98	7.34	7.34×10^3	98.8	0.9
24991-44-13		13-2	A	3.26	7.29	7.29×10^3	100.0	0.4
		13-3	A	3.26	7.29	7.29×10^3	97.5	1.5
		13-4	A	3.26	7.29	7.29×10^3	99.8	0.5
		13-5	A	3.26	7.29	7.29×10^3	98.9	0.9
	2	15-1	B	3.32	7.29	7.29×10^3	98.6	1.4
24991-50-15		15-2	B	3.32	7.29	7.29×10^3	99.8	0.4
		16-1	B	2.94	7.28	7.28×10^3	100.0	0.2
24991-52-16		16-2	B	2.94	7.28	7.28×10^3	100.0	0.8
24991-44-13		13-1	A	3.26	7.29	7.29×10^3	76.1	21.9
24991-54-17		17-1	B	1.20	7.23	7.23×10^3	78.2	19.0
	3	17-2	B	1.20	7.23	7.23×10^3	73.6	23.9
24991-57-18		18-1	B	0.3	7.21	7.21×10^3	-	-
		18-2	B	0.3	7.21	7.21×10^3	70.2	27.4
		18-3	B	0.3	7.21	7.21×10^3	81.9	26.7
24991-71-24	4	24-a	A	2.0	-	-	-	-

(1) Containers 1, 2, and 3 were hot isostatically pressed in a single run.

(2) A - Cold pressed at 30,000 psi ($2.07 \times 10^8 N/m^2$) in a helium-filled die and heated in hydrogen at 2370 F (1570 K) for 3 hours

B - Cold pressed at 30,000 psi ($2.07 \times 10^8 N/m^2$)

(3) Calculated from chromium and thoria X-ray densities and thoria content.

(4) Estimated precision was ± 0.5 percent.

(5) Inconsistent with open porosity measurement and density of sister pellets; probably about 70 to 75 percent dense.

cold pressed without a subsequent hydrogen treatment were transferred from a storage container to the canning assembly for HIP in a dry box. The box was evacuated to high vacuum (10^{-5} torr) ($1.33 \times 10^{-3} N/m^2$) over a two-day period, backfilled with 99.996 percent pure argon, re-evacuated, and backfilled for two more cycles. All HIP container components were cleaned prior to placing in the dry box with an appropriate bright pickle solution* followed by distilled water and absolute-alcohol rinses. One to seven pellets were assembled in tantalum containers. Each pellet was separated from the others by at least one 0.001-in. (2.54×10^{-5}m) tungsten-foil disc and from the container wall by a tungsten-foil sleeve. After the final tungsten-foil disc was in place, the remaining volume of the tantalum tube was filled with Type 304 stainless-steel discs and two tantalum discs.

After assembly, the HIP containers were stored in argon, in double-walled containers, before bringing them out from the dry box. A vacuum furnace was evacuated, backfilled with argon, then opened. The assembled specimens were opened in this atmosphere and loaded into a molybdenum crucible. The period from opening the argon-filled jars until evacuation of the furnace chamber was kept to a minimum. The assemblies were then maintained at 1470 F (1070 K) for 1 hour in a vacuum of 10^{-6} torr ($1.33 \times 10^{-4} N/m^2$). Subsequently, the assemblies were reloaded into jars under argon atmosphere. Each container was then positioned in an electron-beam welding chamber. Again, the time span between opening the jar to atmosphere and evacuation of the chamber was minimized. After a 1-hour evacuation, the upper tantalum disc was welded

*The various pickle solutions used were:
(1) 65 vol % HNO_3 + 35 vol % HF for tantalum
(2) 12 vol % HNO_3 + 38 vol % HF + 50 vol % water for tungsten
(3) 10 vol % HNO_3 + 2 vol % HF + 88 Vol % H_2O for stainless steel

to the tantalum tube to effect a hermetic seal. Each container was subsequently tested for leakage and placed in a close-fitting jacket of 304 stainless steel which also was sealed by an electron-beam weld and checked for leaks.

Nineteen pellets, divided among three containers, were subjected to a hot isostatic-pressing cycle of 2010 F (1370 K) and 10,000 psi ($6.89 \times 10^7 N/m^2$) for a period of two hours. The remaining pellet (No. 24a) was consolidated under identical conditions in a subsequent cycle. Despite double containment in a tantalum inner can and a stainless steel outer can, Container No. 3 failed to maintain a gas-tight-pressure barrier between the pellets and the autoclave atmosphere in the first HIP run. Consequently, the specimens in that container (see Table 4) were not densified.

The resulting product from the HIP cycle, after the container material was removed, was a series of 3/8-in. (9.525×10^{-3}m)-diameter by 1/8-in. (3.75×10^{-3}m)-thick discs.

Density Measurements

The bulk density and open porosity were determined for all pellets except No. 24a, which appeared to be of acceptable density, as indicated by dimensional measurements and metallographic examination. The results of the density measurements are included in Table 4. The successfully consolidated pellets had apparent densities in the range of 98.5 to 100 percent of theoretical and intercommunicating porosity fo 0.0 to 1.5 vol %. The specimens in the container that developed a leak reached a density of about 75 percent of theoretical.

Heat Treatment of Densified Chromium-ThO_2 Pellets

Chromium-ThO_2 pellets, densified by hot isostatic pressing, were heat treated in the apparatus shown in Figure 5. A summary of the heat-treating conditions are included in Table 5. A double-walled tube furnace was used to minimize contamination. An outer helium-purged ceramic tube provided protection for an inner helium-purged molybdenum tube. The molybdenum tube provided an effective shield against possible diffusion of oxygen through the ceramic tube. To provide additional protection, chromium pellets were wrapped in 1-mil (2.54×10^{-5}m)-thick tungsten foil and placed inside a zirconium crucible provided with a lid. In addition to the zirconium crucible, zirconium chips were placed at both ends of the hot zone to getter any contaminants evolved from the stainless steel end fittings. The helium-purge gas was purified with the same zirconium-sponge getter used for purification of the helium fed to the chromium-ThO_2 powder preparation unit. The fact that chromium-ThO_2 powder was prepared with nitrogen in the range of 10 to 20 ppm is good evidence that the getter was effective.

The closed container for the pellets was considered to be a necessary precaution, not only for gettering of contaminants but also as a precaution against excessive evaporation of chromium during the 100-hour heat treatments at 2400 and 2600 F (1590 and 1700 K). The effectiveness of the method is indicated by the fact that only 1 to 3 mils (2.54×10^{-5} to 7.62×10^{-5}m) of chromium was lost by evaporation and that the ThO_2 residue left on the surface of the pellets after evaporation of chromium was white in color. Trace amounts of oxygen contamination would be expected to leave a green residue of Cr_2O_3 in the ThO_2.

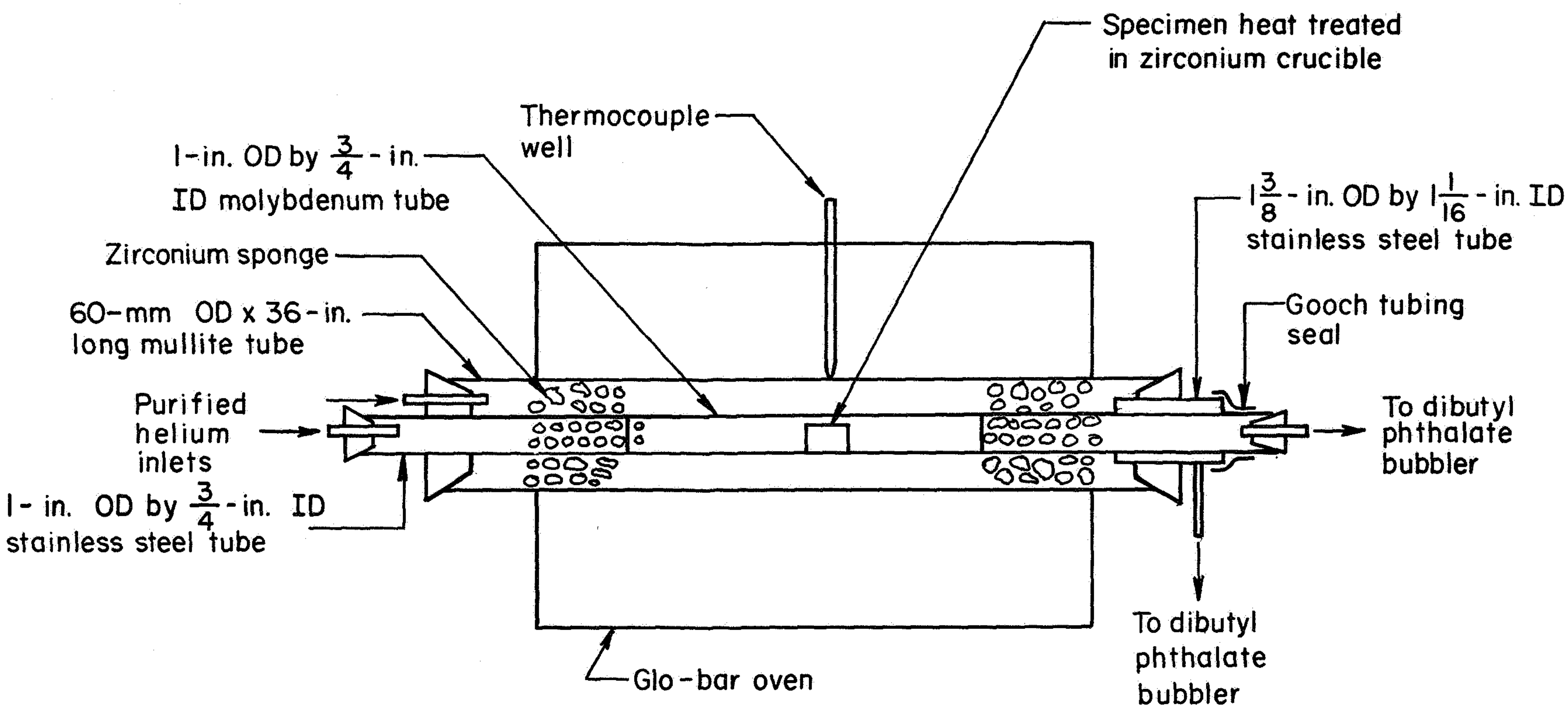


FIGURE NO. 5. APPARATUS FOR HEAT TREATING CONSOLIDATED CHROMIUM-ThO_2 POWDER

TABLE 5. SUMMARY OF HARDNESS DATA ON CONSOLIDATED CHROMIUM-ThO_2 PELLETS

Run No.	ThO_2 Concn, vol %	Pellet No.(1)	Vickers Hardness Number, 10-Kg Load: As-Consolidated(2)		After Heat Treating for 100 Hr(3): 2400 F (1590 K)	2600 F (1700 K)
24991-38-11	2.0	11-1	219		207	-
		11-2	223	(228)	-	402
24991-41-12	5.0	12-1	216		-	-
		12-2	226	(251)	-	425
		12-3	222		216	-
24991-44-13	3.3	13-2	212		-	-
		13-3	221		-	-
		13-4	224	(229)	-	-
		13-5	238		-	-
24991-50-15	3.3	15-1	261		-	-
		15-2	245	(269)	-	-
24991-52-16	2.9	16-1	241	(253)	-	238
		16-2	254		-	-
24991-71-24	2.0	24-1	208		-	-
		24-2	-		-	160
		24-3	-		180	-

(1) Pellets were separated with tungsten foil during hot isostatic pressing of Pellets 11-1 through 16-2. With Pellets Nos. 24-1 through 24-3, the tungsten-foil separator was not used, and a single ingot was obtained. The ingot was cut into three sections, with the center section numbered 24-2. The indicated groups of pellets were consolidated in a single container.

(2) Average of three determinations on polished surface. Independent checks on hardness were made by a second operator on selected specimens.

(3) The indicated groups of pellets were heat treated simultaneously in a tungsten-lined zirconium container.

Hardness of Consolidated and Heat-Treated Chromium-ThO_2

Hardness data were obtained for as-hot isostatically pressed and heat-treated chromium-ThO_2 pellets as summarized in Table 5. The Vickers Hardness Numbers for the as-consolidated material are in the range of 208 to 269 VHN, which is considerably harder than the range of 120 to 140 VHN obtained for high-purity iodide chromium. Since the chromium-ThO_2 is nearly as pure as iodide chromium with respect to the hardening contaminants nitrogen (10-20 ppm), carbon (10-20 ppm), and sulfur (<100 ppm), it is not believed that the high hardness is a result of interstitial impurities rather than the ThO_2 addition. Although the amount of oxygen contamination as Cr_2O_3 is uncertain, it is not a significant hardner for chromium, as evidenced by the fact that the hardness of laboratory-grade electrolytic chromium containing 5000-ppm oxygen is in the range of 130 to 160 VHN. Therefore, it appears to be justifiable to attribute the high hardness to (1) residual stresses resulting from hot isostatic pressing, (2) stresses induced by the presence of ThO_2 particles, and (3) an assumed fine-grain size*. Relief of stresses and grain growth could account for decreases in hardness obtained for five of the seven pellets on heat treating (see Table 5). However, a substantial increase in hardness (increases of 179 and 199 VHN for Pellets Nos. 11-2 and 12-2, respectively) for two of the pellets is difficult to explain. Contamination does not appear to be an only cause, since the two pellets that increased in hardness were heat treated simultaneously,

*Etchants normally used to reveal grain boundaries in chromium metal were found to be unsatisfactory for the chromium-ThO_2, as a result of excessive attack around ThO_2 particles. A suitable etchant was not identified.

and in the same container, with Pellet No. 16-1 which did not increase in hardness. Since Pellet No. 16-1 has a ThO_2-concentration (2.9 vol %) intermediate with the two that increased in hardness (11-2 with 2.0 vol % ThO_2 and 12-2 with 5 vol %), the gross amount of ThO_2 alone does not indicate a valid explanation for the hardness differences.

METALLOGRAPHIC EVALUATION OF CHROMIUM-ThO_2

Metallographic evaluation was concluded for a variety of specimens described in the following list.

(1) As-prepared chromium-ThO_2 powder.

(2) Chromium-ThO_2 powder, hydrogen heat treated at 1470 F (1070 K) for four hours to remove residual CrI_2.

(3) Same as (2) for material that was cold pressed at 30,000 psi ($2.07 \times 10^8 N/m^2$), and hydrogen sintered at 2370 F (1570 K) for three hours.

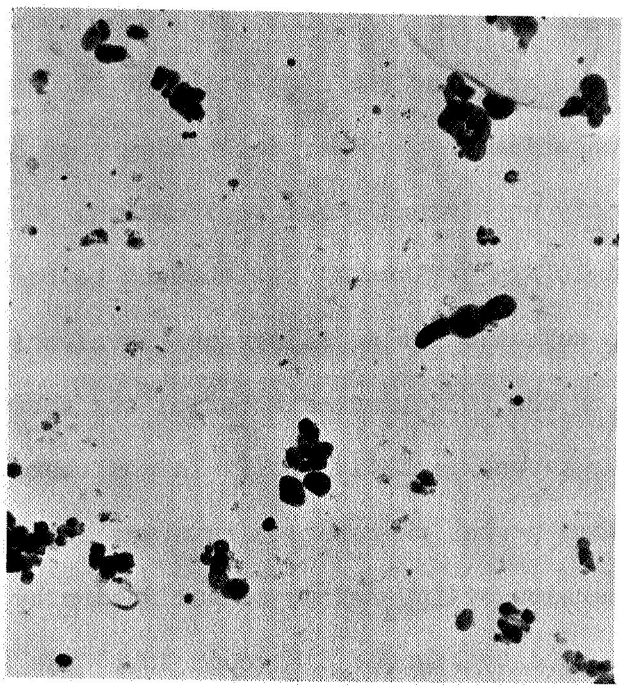
(4) Same as (3) for material cold pressed at 400,000 psi ($2.76 \times 10^9 N/m^2$).

(5) Same as (3) for material hot isostatically pressed.

(6) Same as (2) for material cold pressed at 30,000 psi ($2.07 \times 10^8 N/m^2$) and hot isostatically pressed.

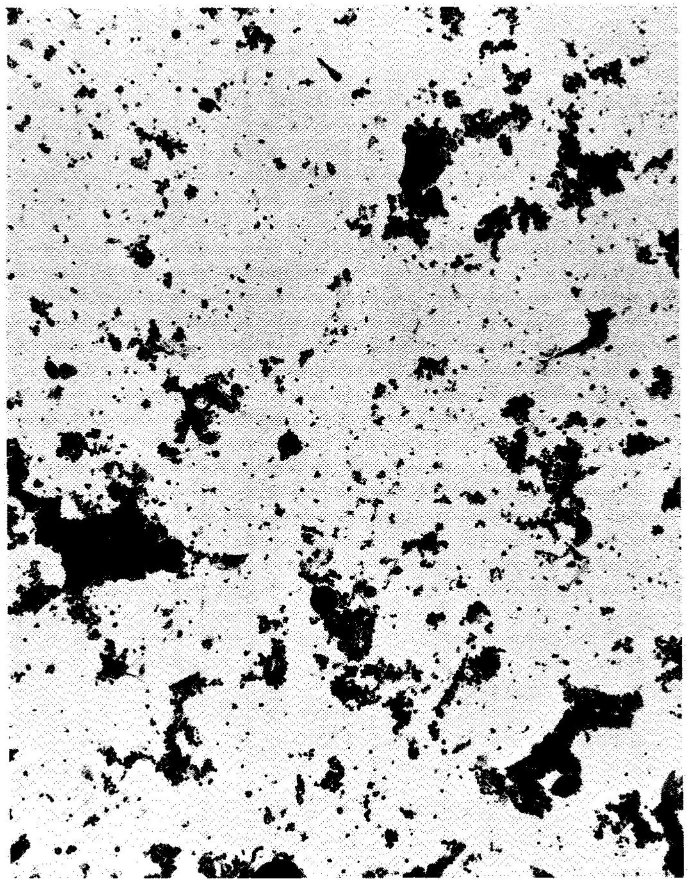
(7) One hundred hours heat-treated products of (5) and (6).

Typical examples of (1) and (2) are shown in Figures 3 and 4 and discussed in the section entitled "Preparation of Chromium-ThO_2 Powder". Results of extraction replication of material (Preparation Run No. 24991-33-10), described in Item (3) and containing 1.6 vol % ThO_2, are shown in Figure 6. It is interesting to note that the material sintered in hydrogen at 2370 F (1570 K) to a density sufficient for metallographic evaluation and that the dispersion of ThO_2 is good. Subsequent preparations of chromium-ThO_2 powder containing 2 to 5 vol % ThO_2 did not densify sufficiently on sintering for replication. Cold pressing at 400,000 psi ($2.76 \times 10^9 N/m^2$) (Item 4) was thought to be a convenient method for densification suitable for metallographic evaluation. Examples of the results obtained on the cold-pressed material are shown in Figure 7. The dispersion of ThO_2 is unexpectedly poor. In contrast, material (Items 5 and 6) from the same powder preparation runs was found to contain a relatively good dispersion of ThO_2 after consolidation by hot isostatic pressing, as indicated by Figures 8 through 10b. The fact that extraction replication was used for the cold-pressed material, while direct replication was used for the hot isostatically pressed material, does not account for the difference in results. The results of the direct-replication method were compared to that obtained with the extraction-replication method on the cold-pressed material, as well as the hydrogen-sintered material (Item 3), and were found to be in good agreement. Therefore, the difference in the dispersion obtained in the cold-pressed and the isostatically pressed material is attributable to the method used for densification.



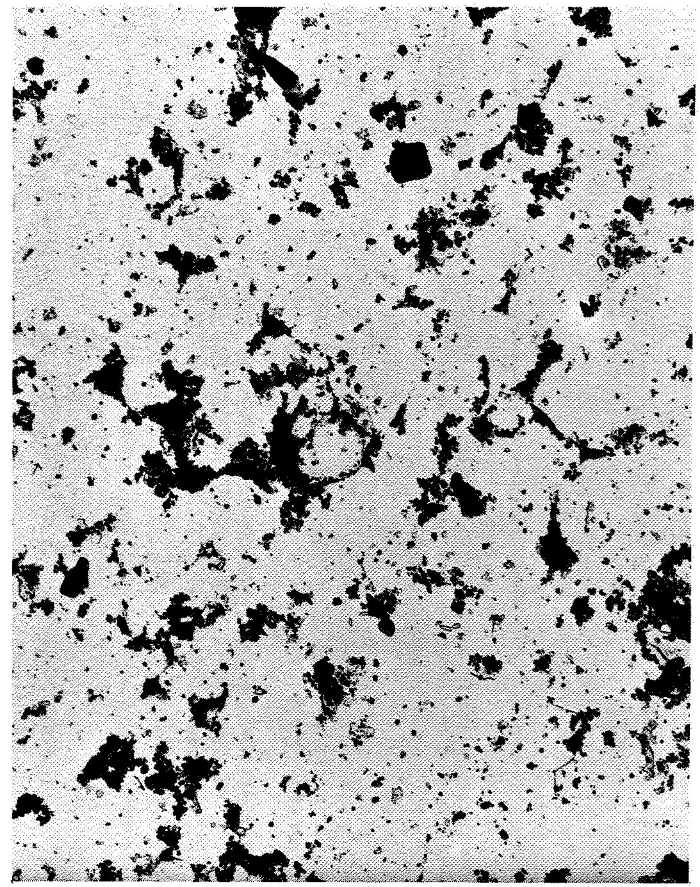
30,000X EH-993

FIGURE NO. 6. EXTRACTED PARTICLES FROM CHROMIUM-ThO_2 POWDER DENSIFIED ON SINTERING AT 2370 F (1570 K) IN HYDROGEN (Powder Preparation No. 24991-33-10)



7500X 1μ EH-1045

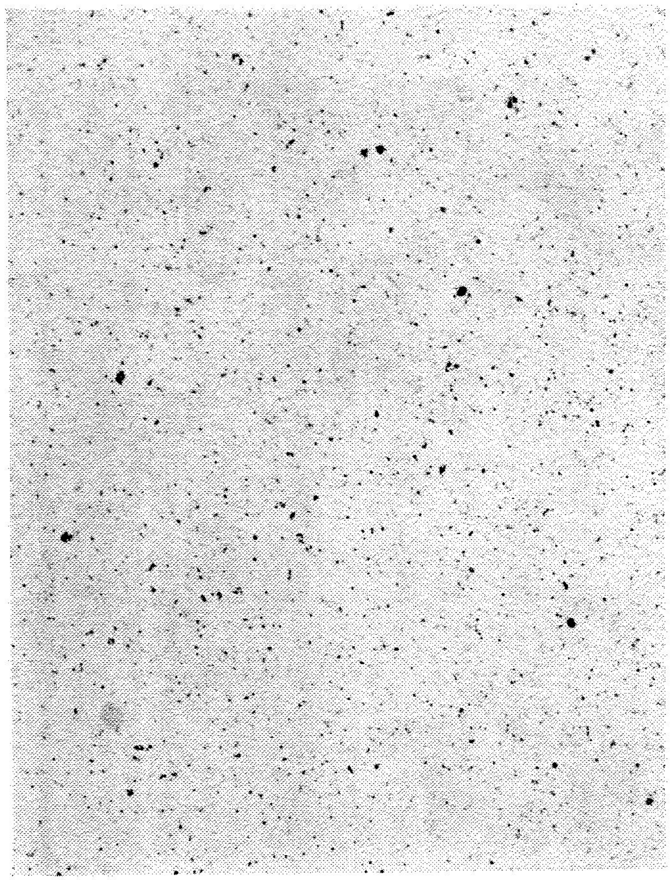
(Powder Preparation No. 24991-50-15, 3.3 vol % ThO_2)



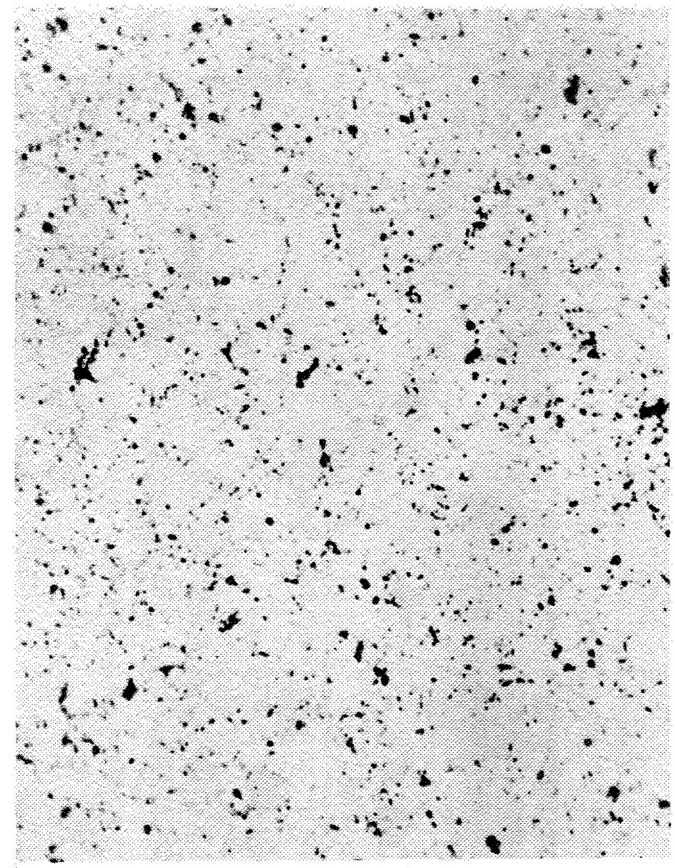
7500X 1μ EH-1046

(Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2)

FIGURE NO. 7. EXTRACTED PARTICLES AND AGGLOMERATES FROM CHROMIUM-ThO_2 POWDER COLD PRESSED AT 400,000 PSI (2.76x $10^9 N/m^2$)

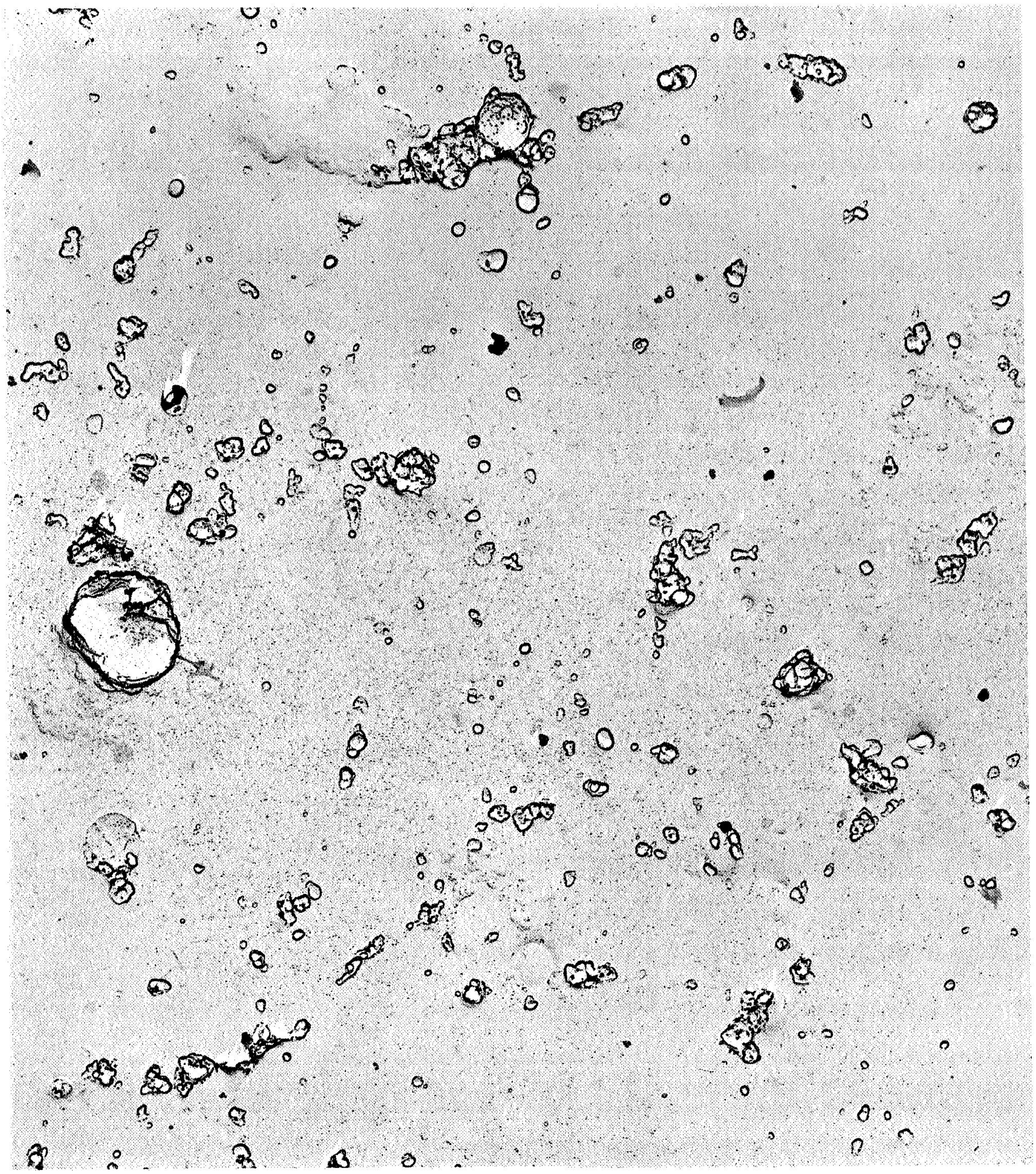


250X 9C583



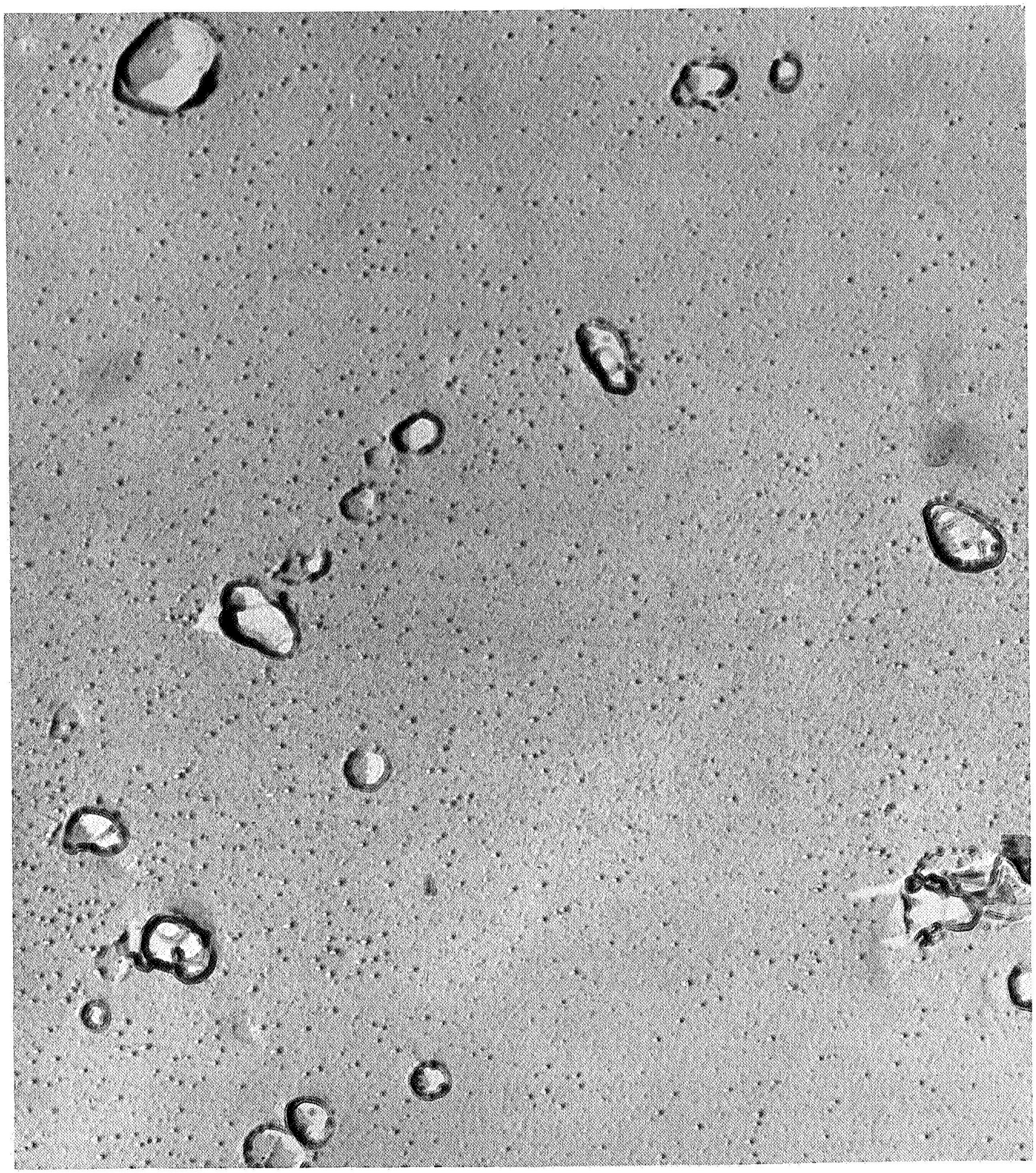
1000X 9C588

FIGURE NO. 8. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)



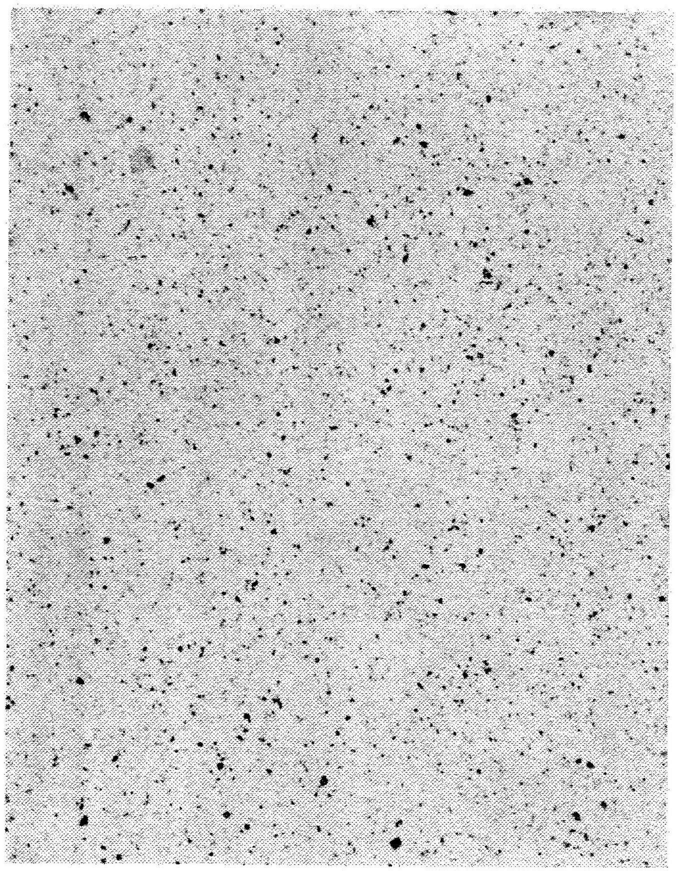
10,000X $\underline{1\mu}$ EH-1241

FIGURE NO. 8A. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)

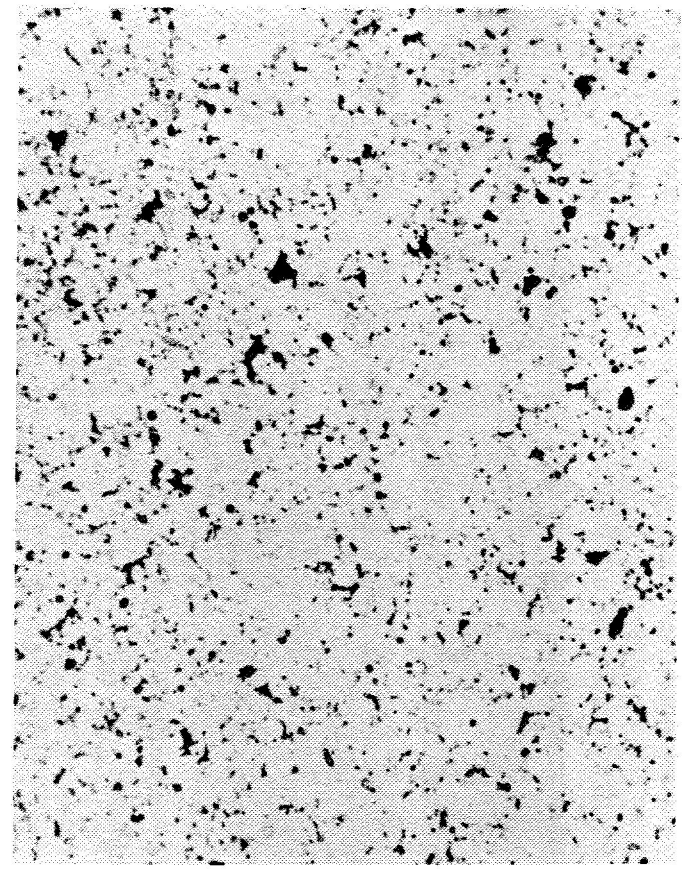


50,000X — 1μ — EH-1242

FIGURE NO. 8B. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)

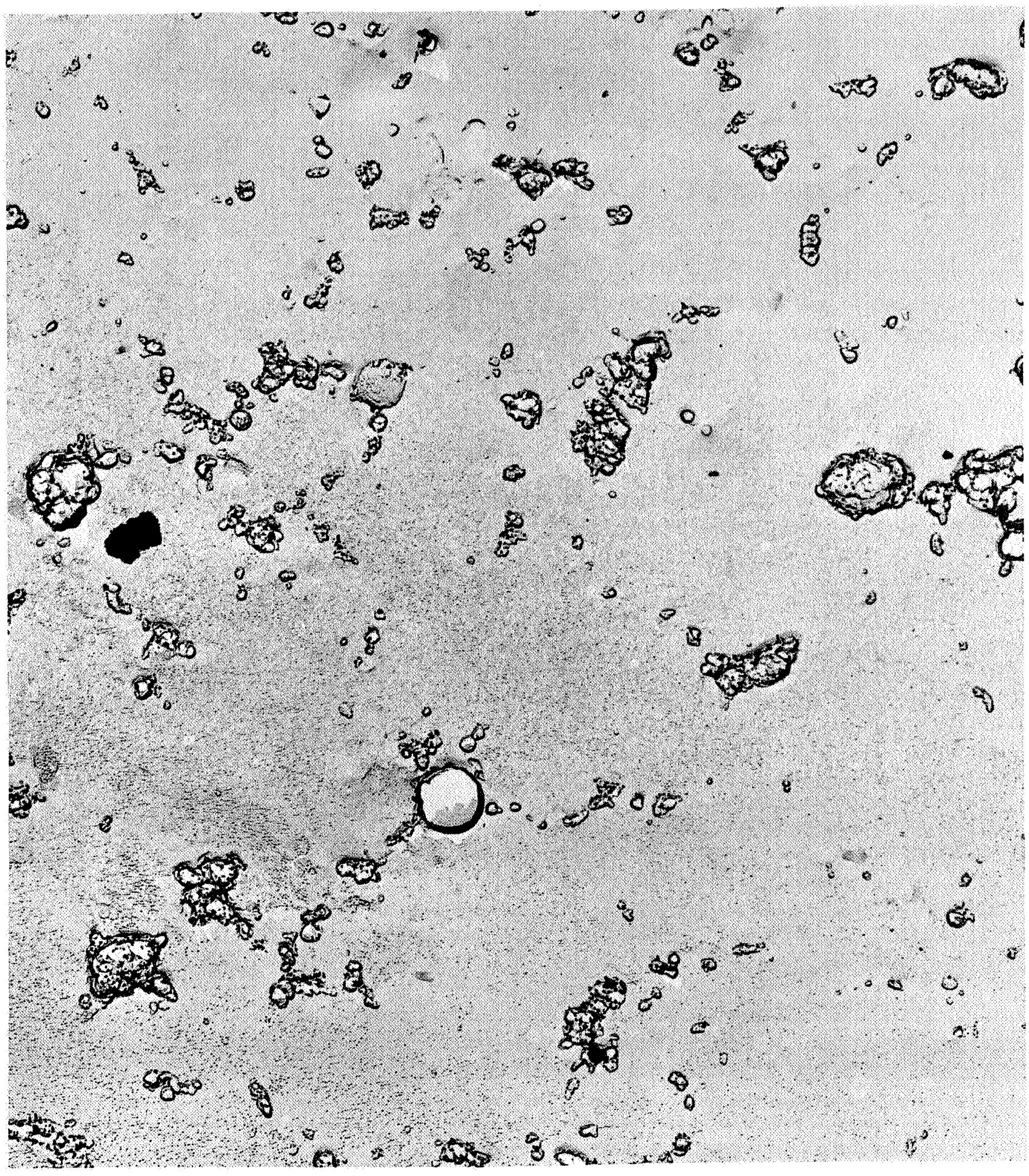


250X 9C584



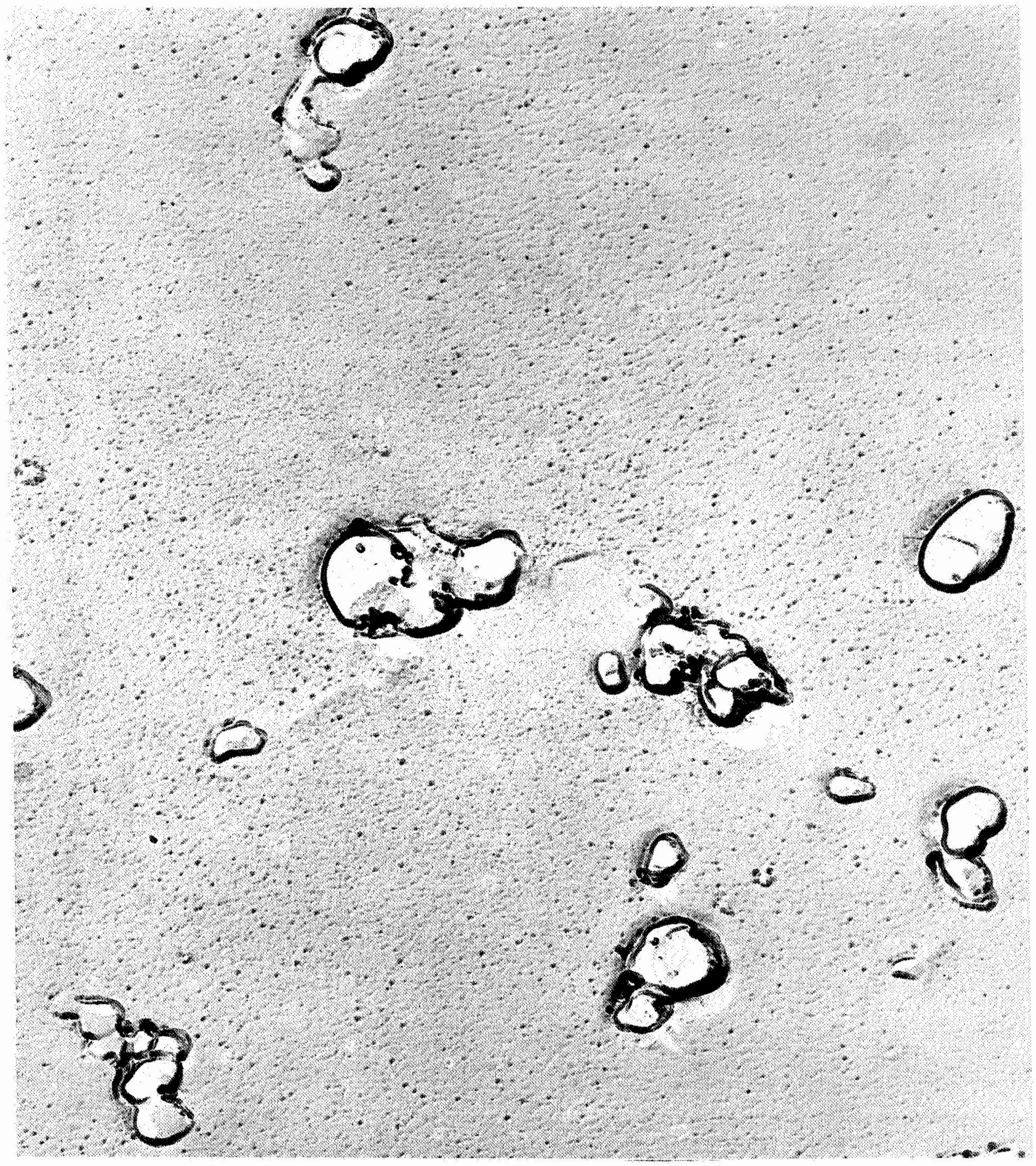
1000X 9C589

FIGURE NO. 9. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)



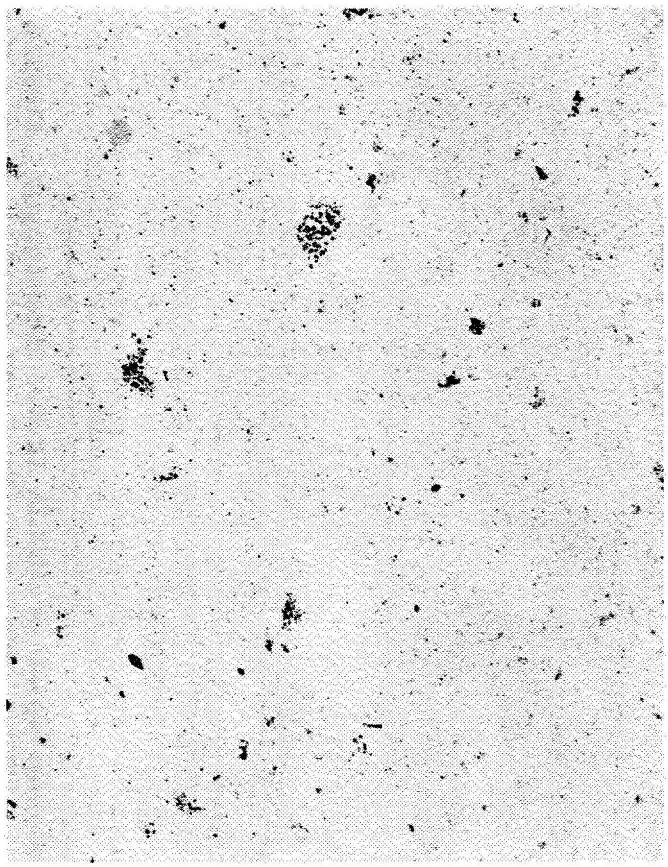
10,000X 1μ EH-1245

FIGURE NO. 9A. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)

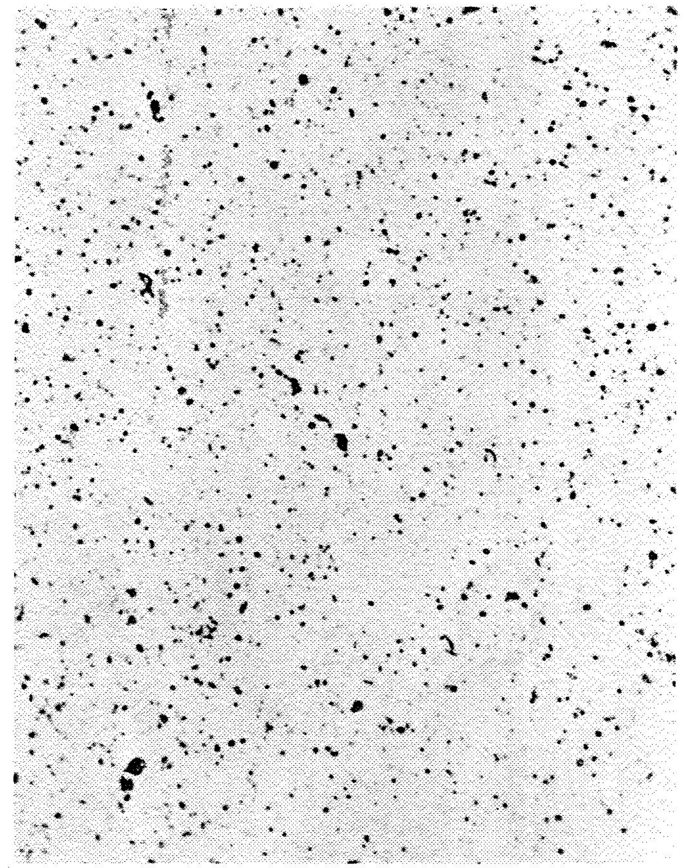


50,000X　　　　1μ　　　　EH-1246

FIGURE NO. 9B. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)

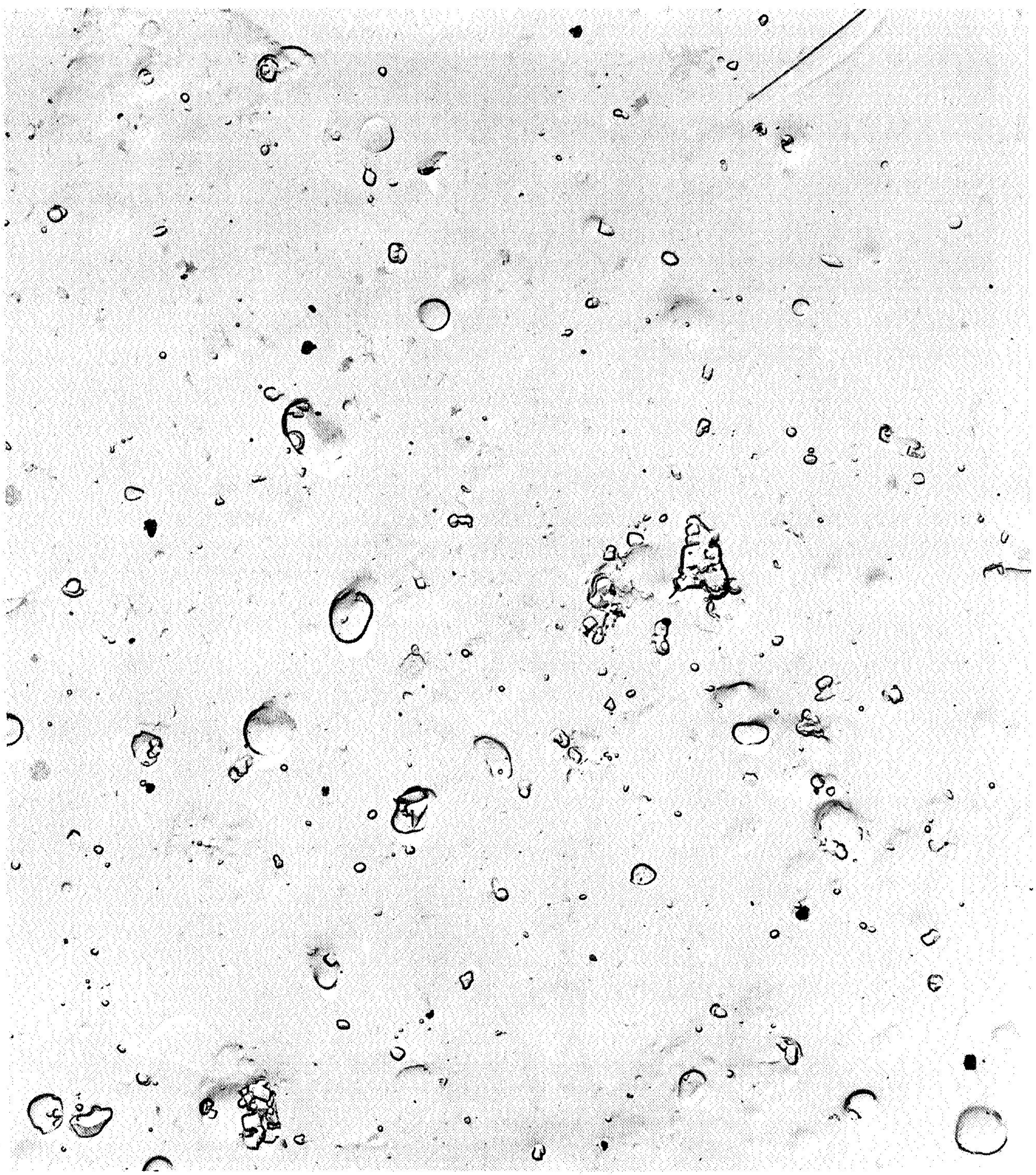


250X 9C587



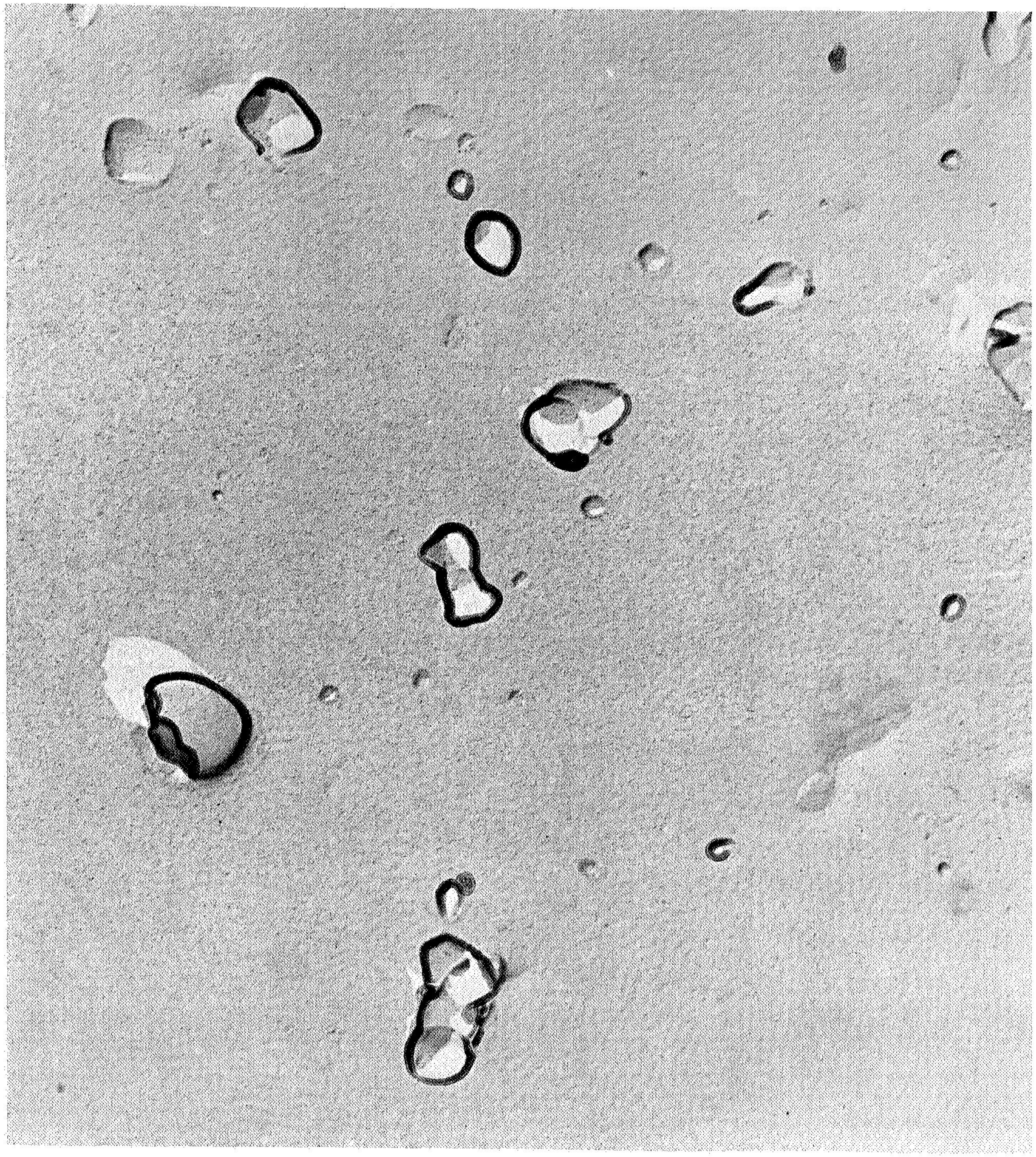
1000X 9C592

FIGURE NO. 10. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2 (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)



10,000X 1μ EH-1243

FIGURE NO. 10A. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)



50,000X 1μ EH-1244

FIGURE NO. 10B. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)

There appears to be no significant difference in the dispersion of ThO_2 in material that either was sintered (Item 5) (see Figures 8 through 9B and 11 through 11B) or not sintered (Item 6) (see Figures 10 through 10B) in hydrogen 2370 F (1570 K) for three hours prior to hot isostatic pressing.

The dispersion of ThO_2 was nearly identical for the consolidated chromium-ThO_2 powder prepared from the two ThO_2 powder feed materials used in this investigation. The consolidated material shown in Figures 8 through 10B was prepared with a free-flowing fused ThO_2 powder, while the consolidated material shown in Figures 11 through 11B was prepared from an agglomerated ThO_2 which was dispersed in water and freeze-dried.

Results of metallographic examinations of material (Item 7) heat treated for 100 hours at 2400 and 2600 F (1590 and 1700 K) to gain information on thermal stability of the dispersion are shown in Figures 12 through 18B. A comparison of the metallography on the as-pressured-bonded (Figures 8 through 11B) and the heat-treated material (Figures 12 through 18B) indicate that clumps of ThO_2 coalesced to form spherical particles at 2600 F (1700 K) (see Figures 15 through 18B) and are in a stage of transition from clumps to spheres in the material heat treated at 2400 F (1590 K) (see Figures 12 through 14B). However, a decrease in the dispersion of particles is not evident on comparison of Figures 8 through 11B with Figures 12 through 18B.

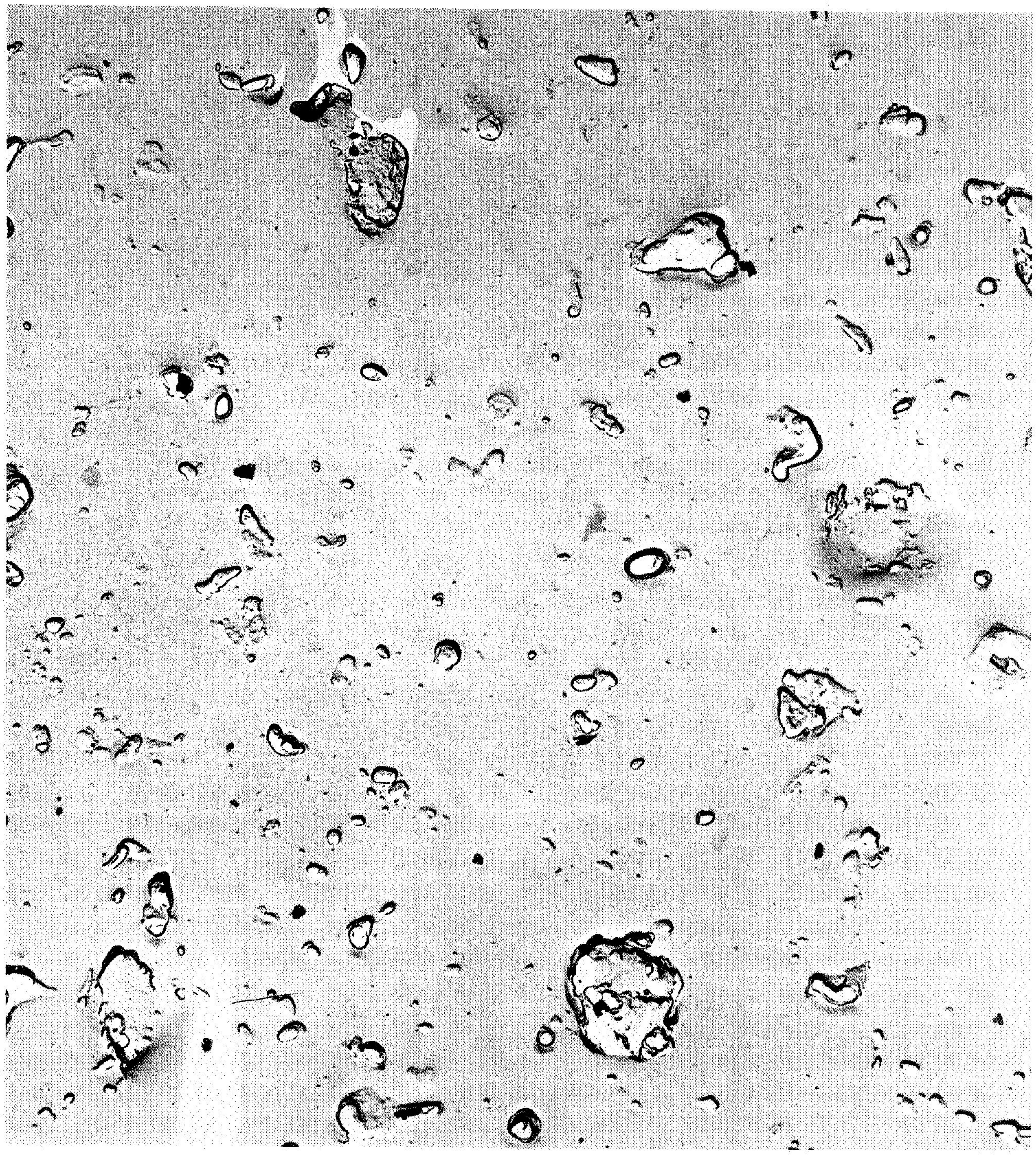
Lineal Analysis* performed on electron micrographs taken at 10,000X confirm that the dispersions are stable. The results of the

*The mean interparticle spacing (IPS) was determined by the random line intercept method method described by Fullman (Trans. AIME, 197, 1953, p. 447). The length of traverse used in the measurements was 120 microns (1.2×10^{-4}m).

250X 3D408

1000X 3D411

FIGURE NO. 11. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2
(Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2
Pellet No. 24-1)



10,000X $\underline{1\mu}$ EH-1482

FIGURE NO. 11A. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-1)

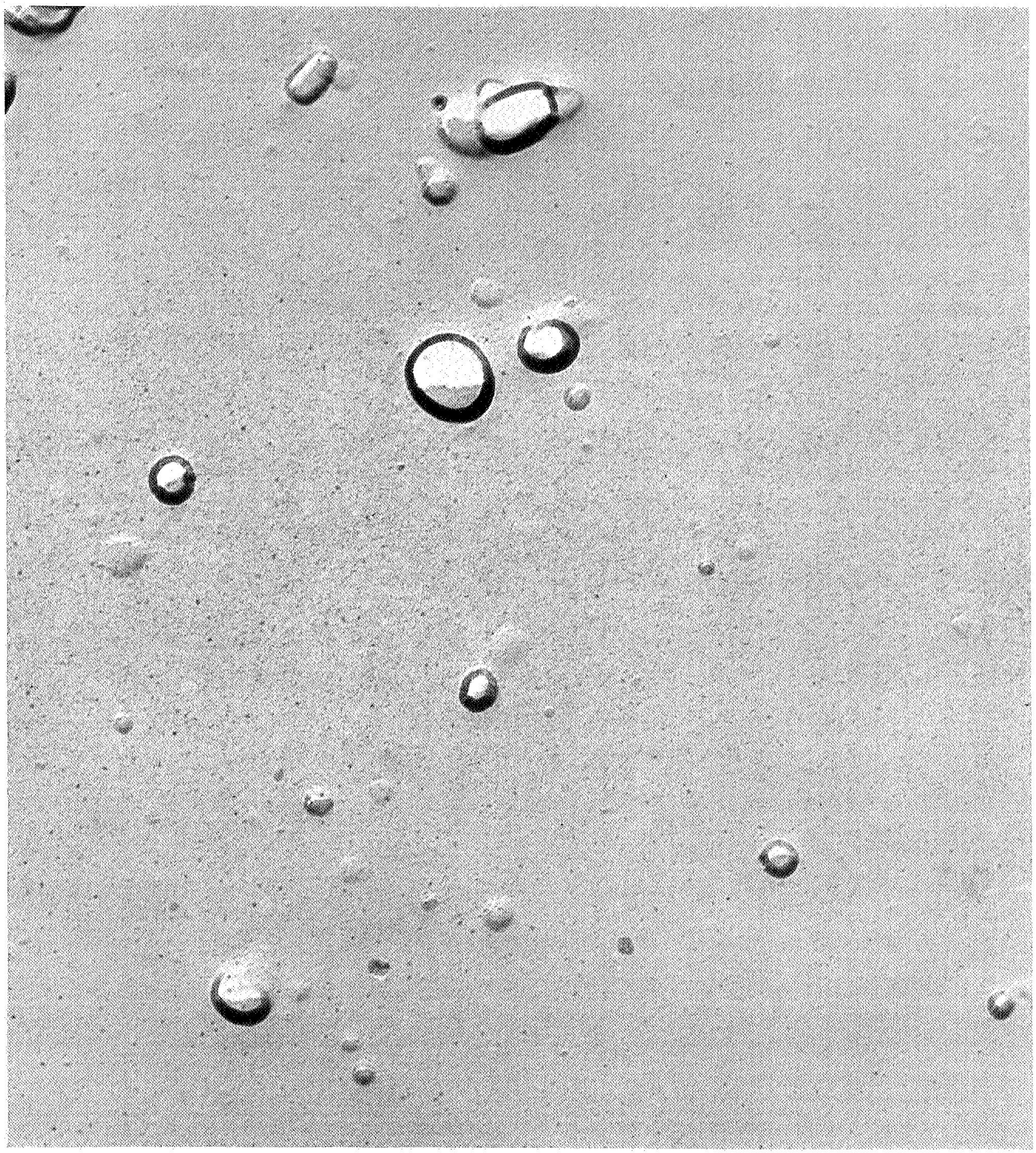
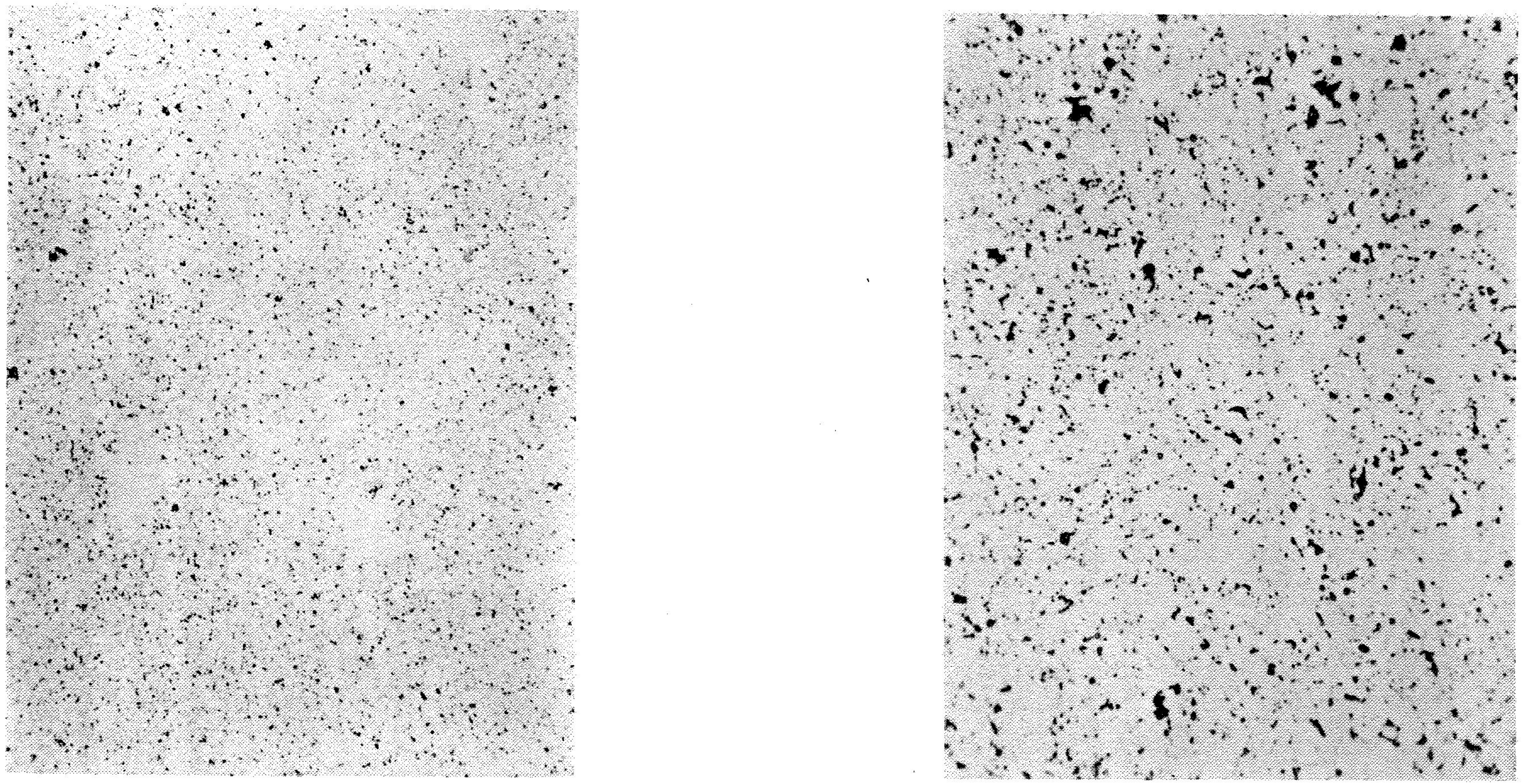
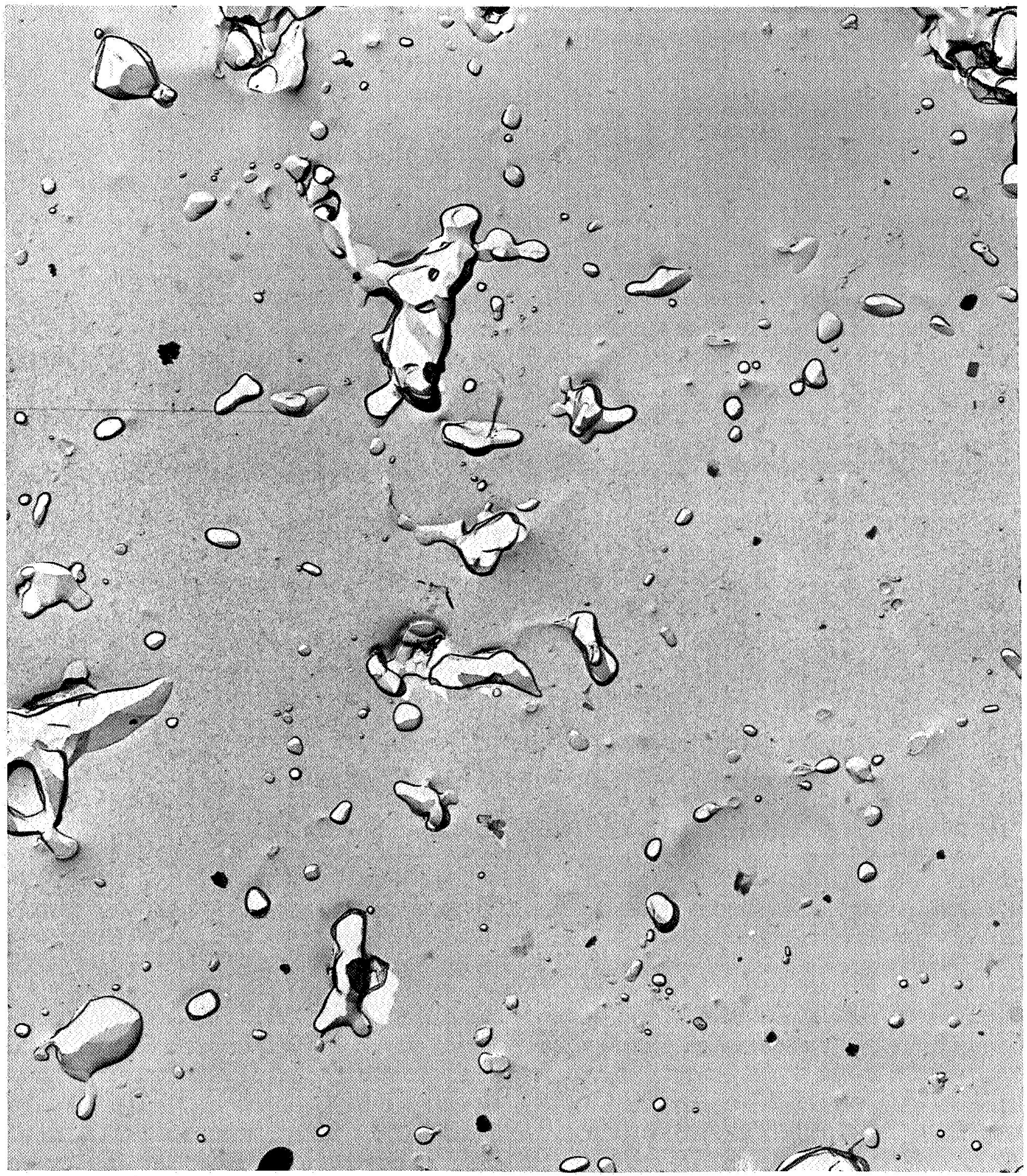


FIGURE NO. 11B. DISPERSION OF THORIA IN HOT ISOSTATICALLY PRESSED CHROMIUM-ThO_2. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-1)



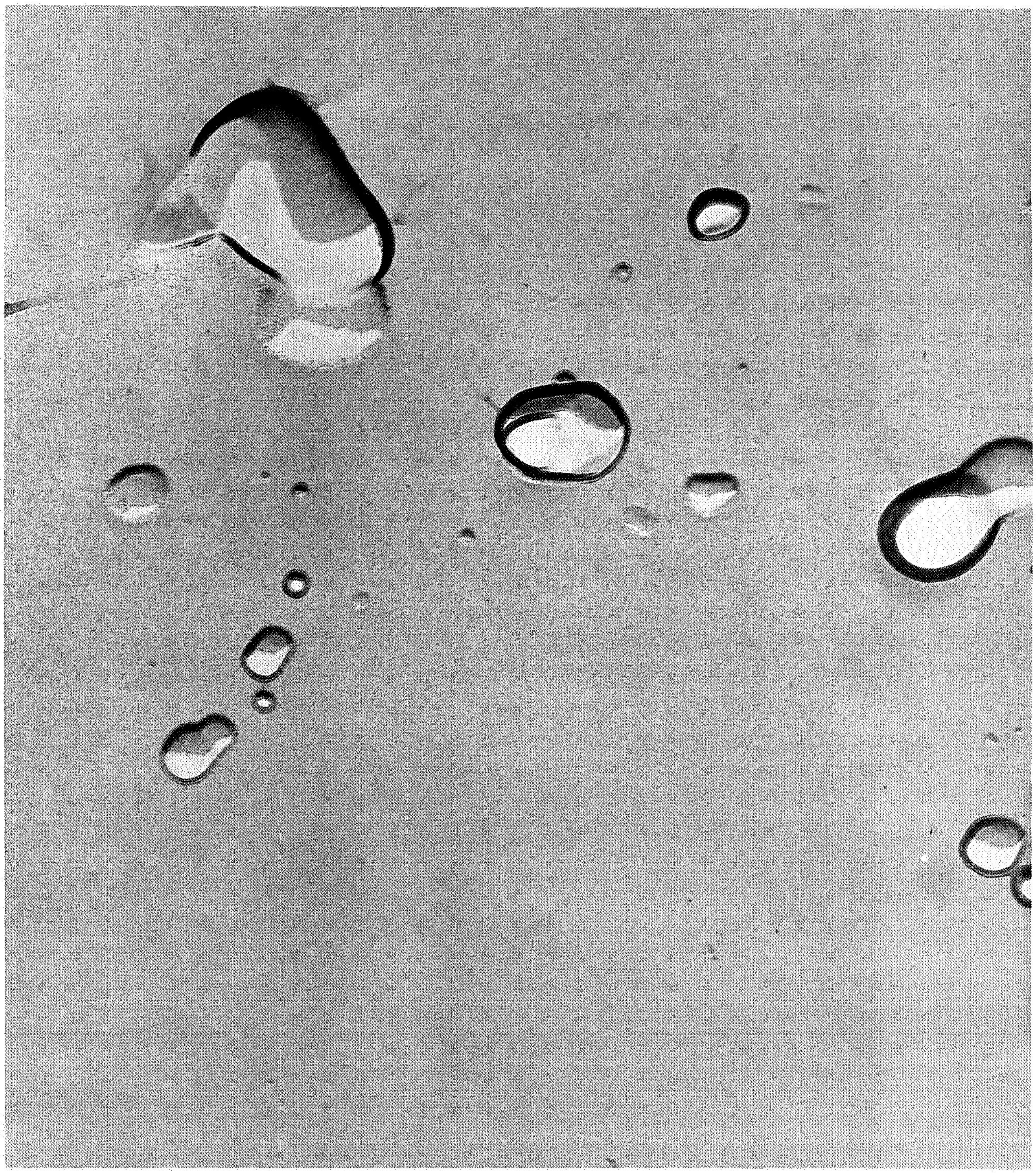
250X 1D418 1000X 1D423

FIGURE NO. 12. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-1)



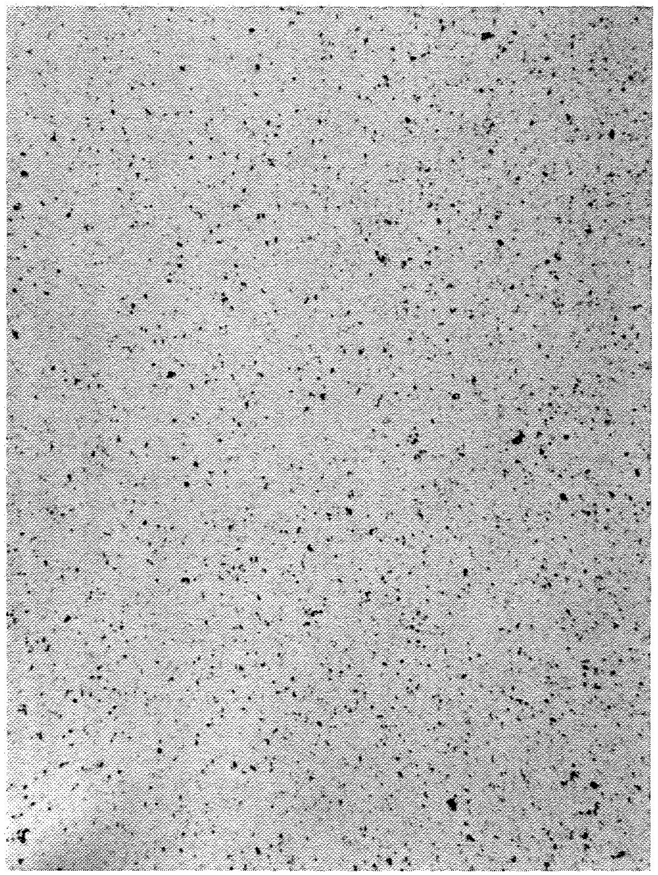
10,000X 1μ EH-1159

FIGURE NO. 12A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-1)

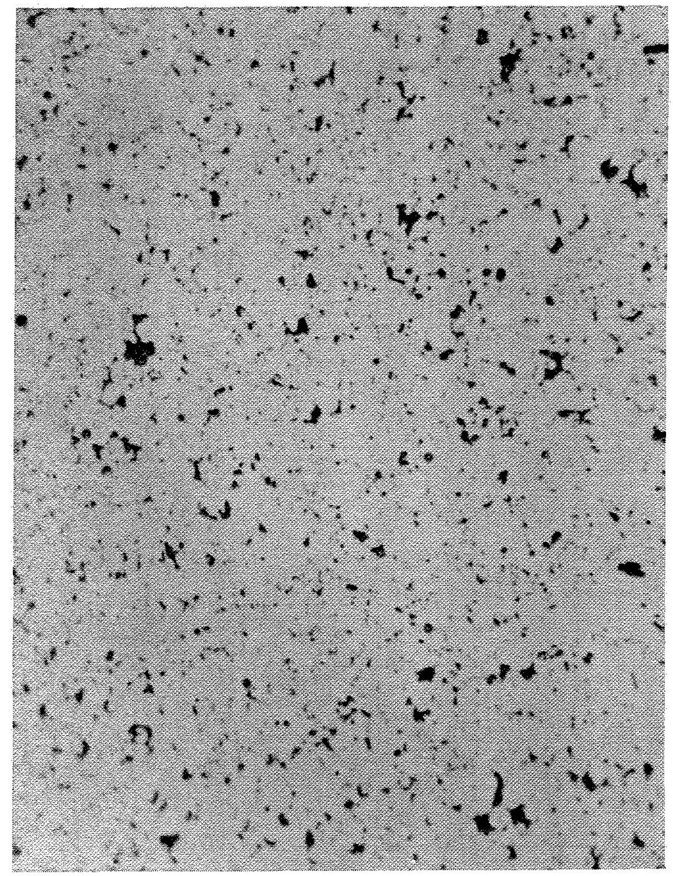


50,000 1μ EH-1160

FIGURE NO. 12B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-1).

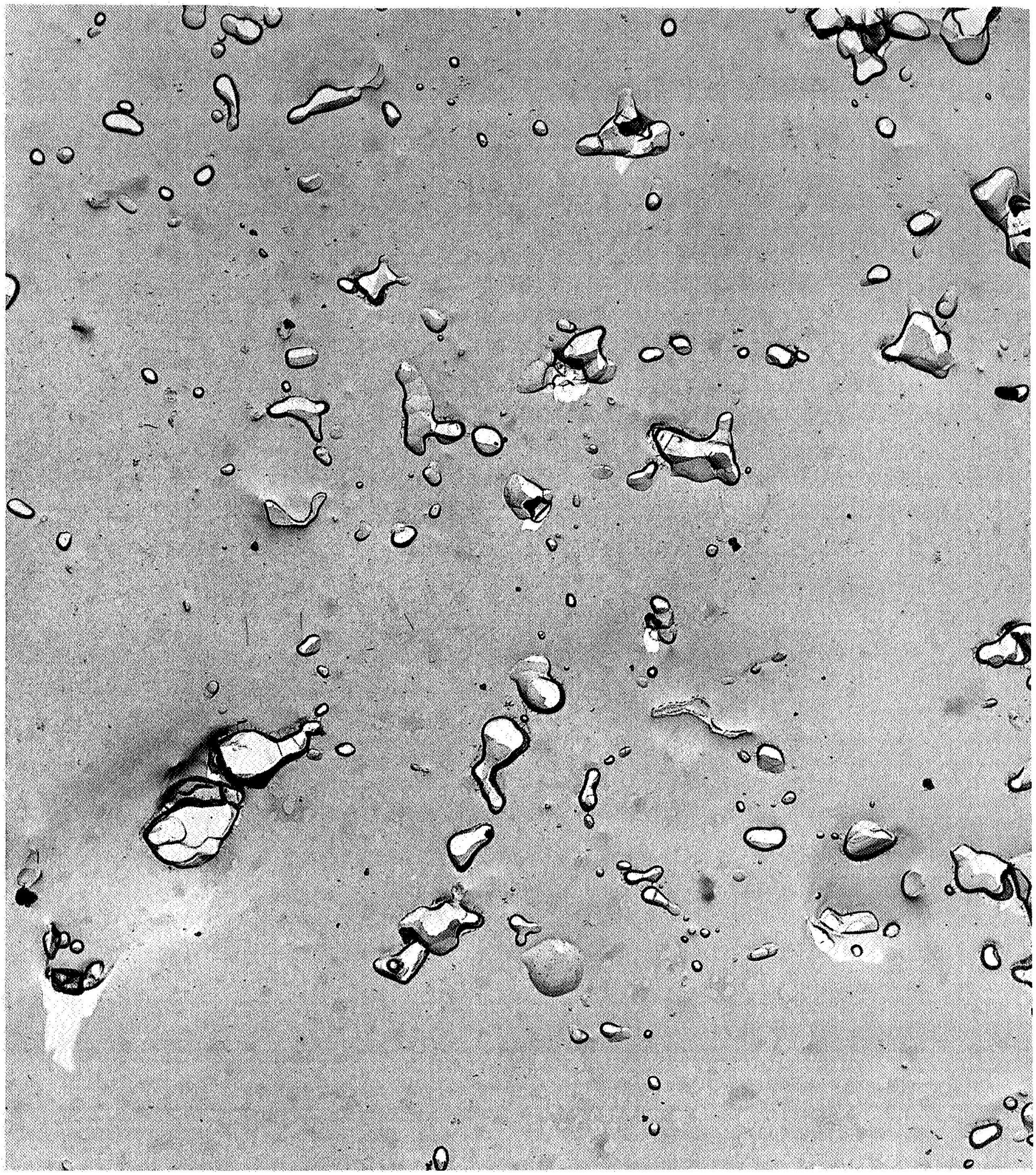


250X 1D419



1000X 1D424

FIGURE NO. 13. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-3)



10,000X | 1μ | EH-1161

FIGURE NO. 13A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-3)

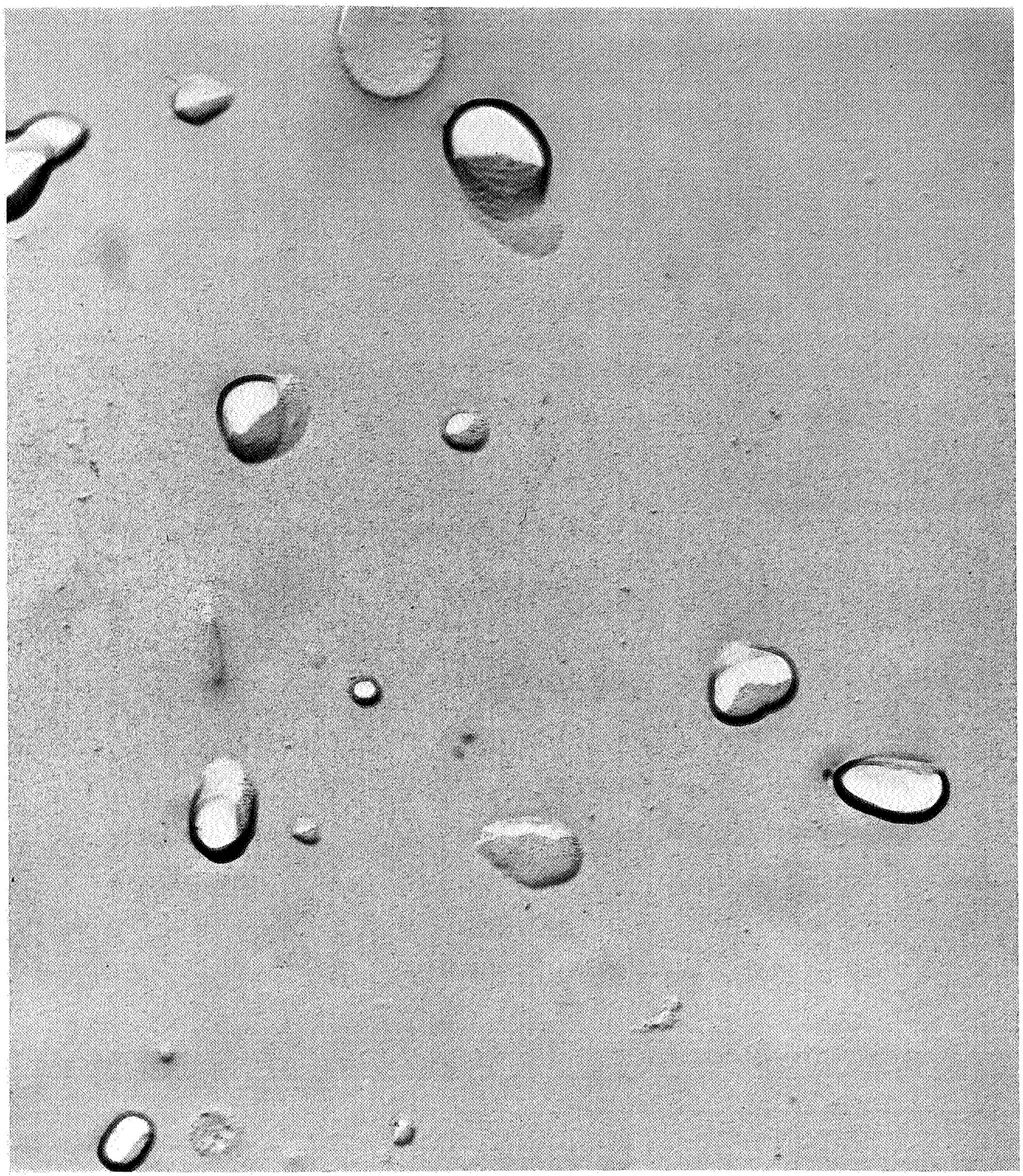
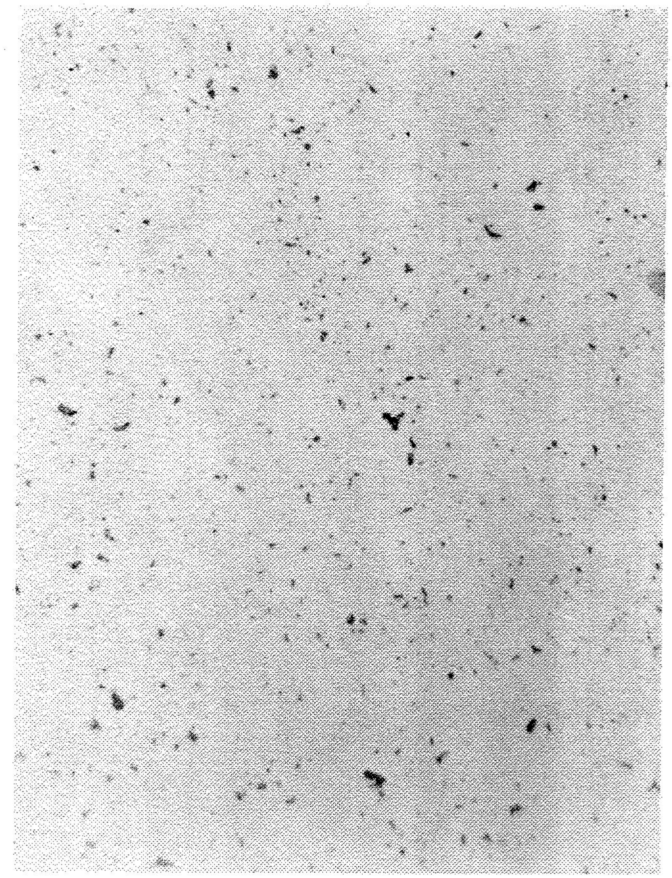


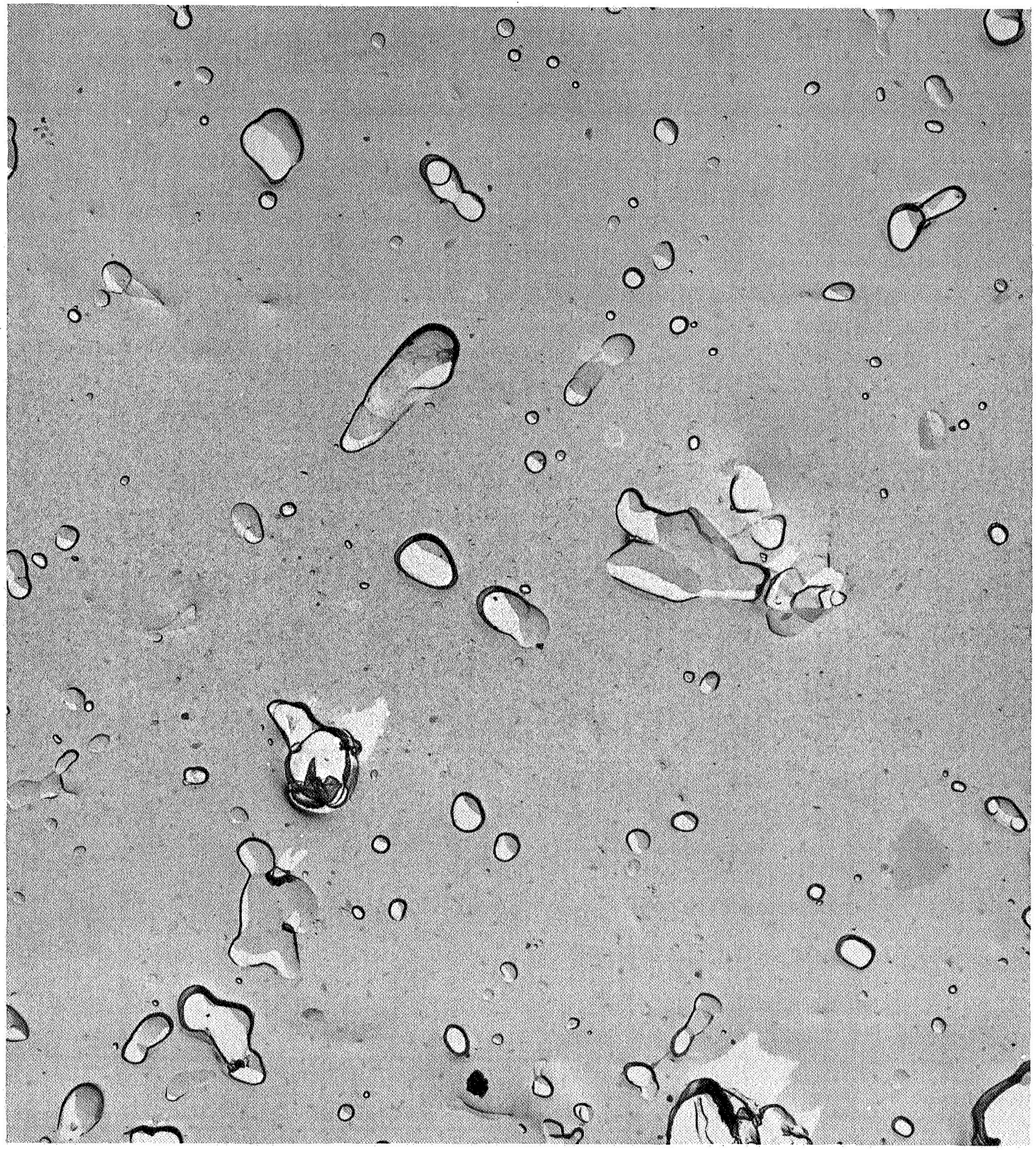
FIGURE NO. 13B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-3)

250X 3D410



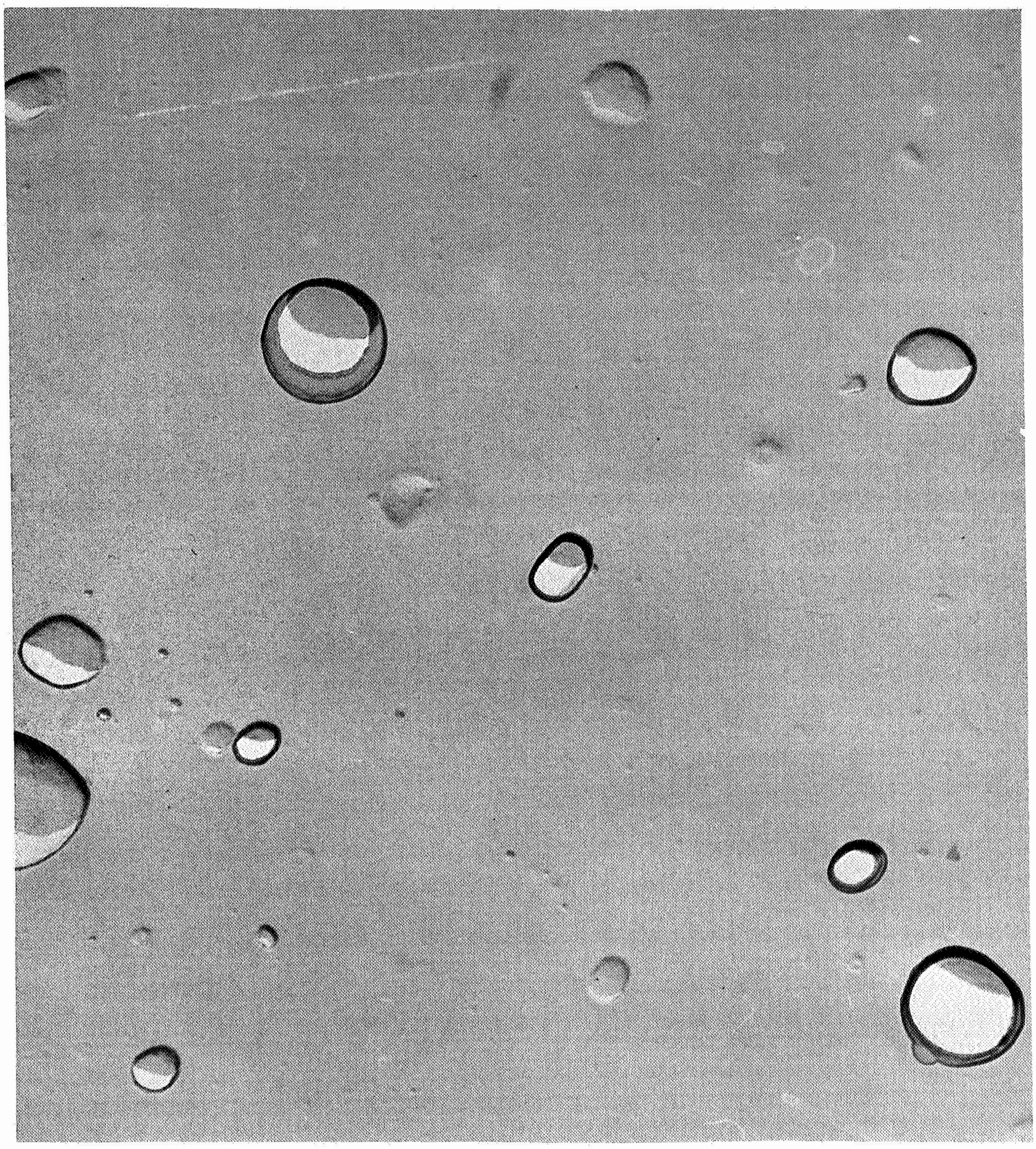
1000X 3D413

FIGURE NO. 14. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-3)



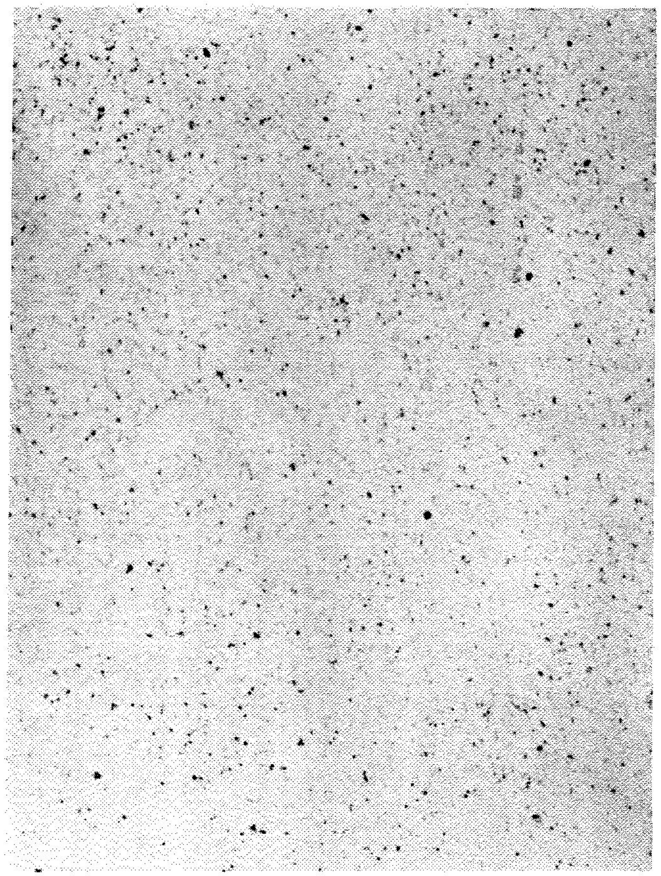
10,000X 1μ EH-1484

FIGURE NO. 14A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-3)

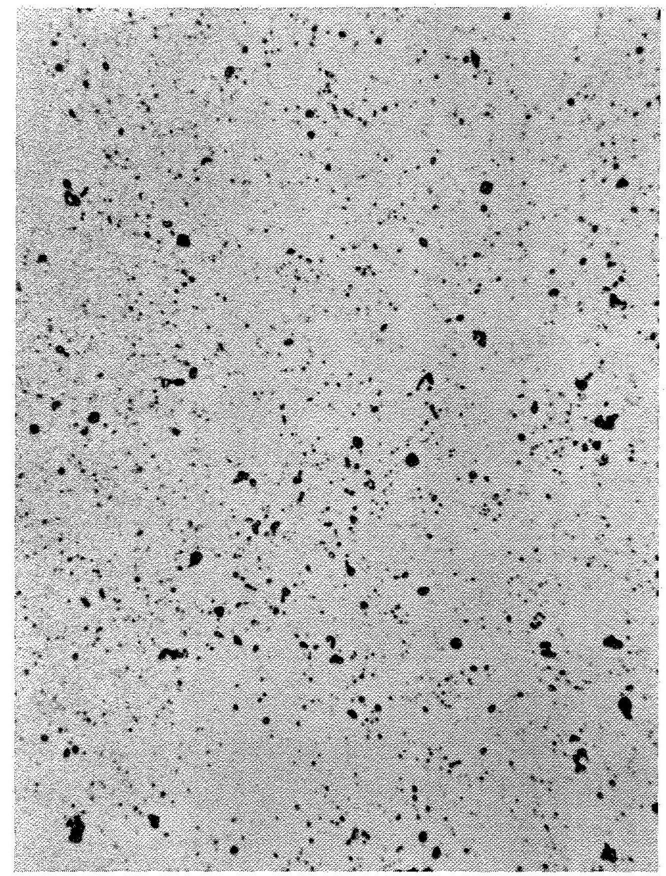


50,000X 1μ EH-1485

FIGURE NO. 14B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2400 F (1590 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-3)

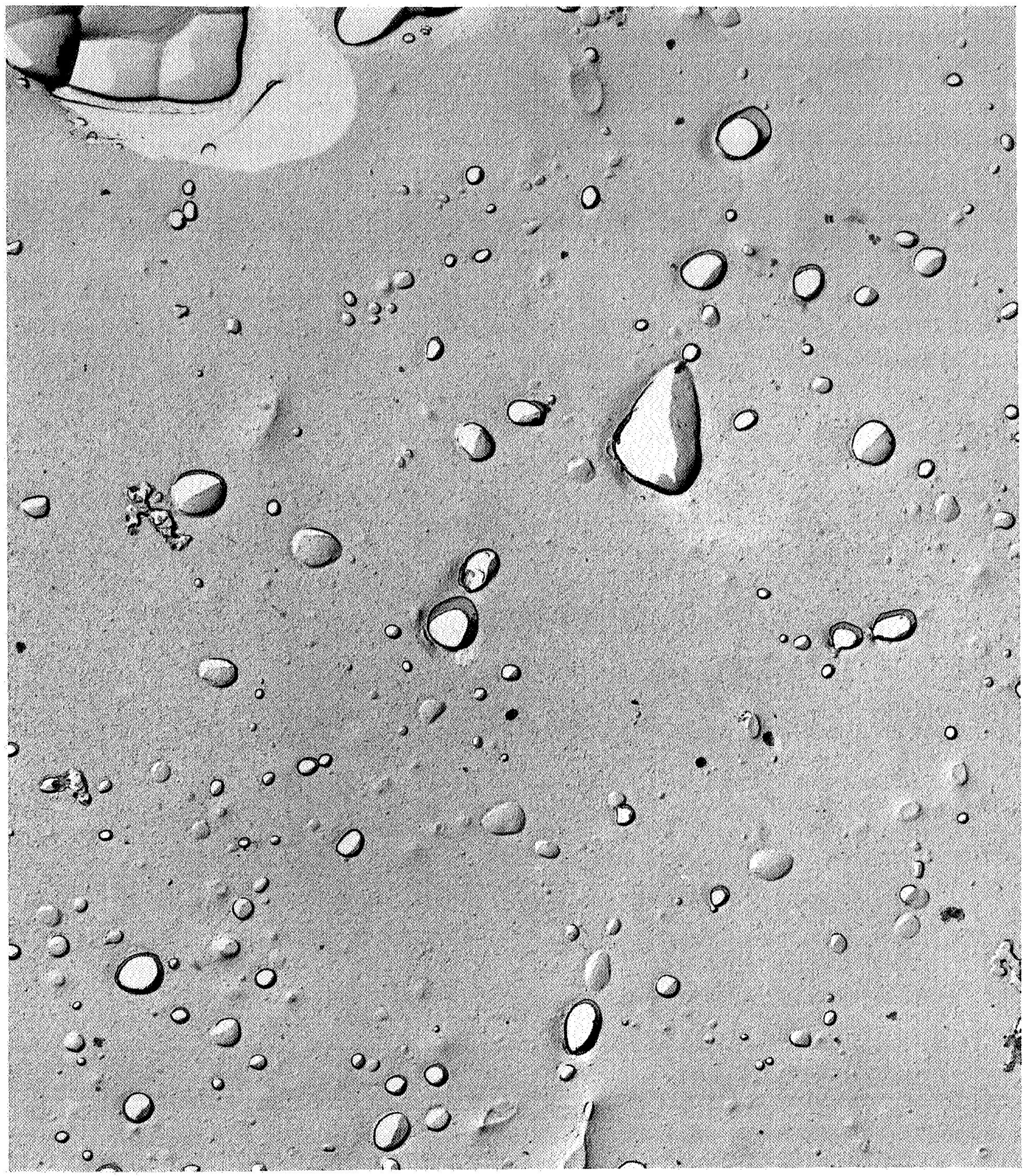


250X 1D416



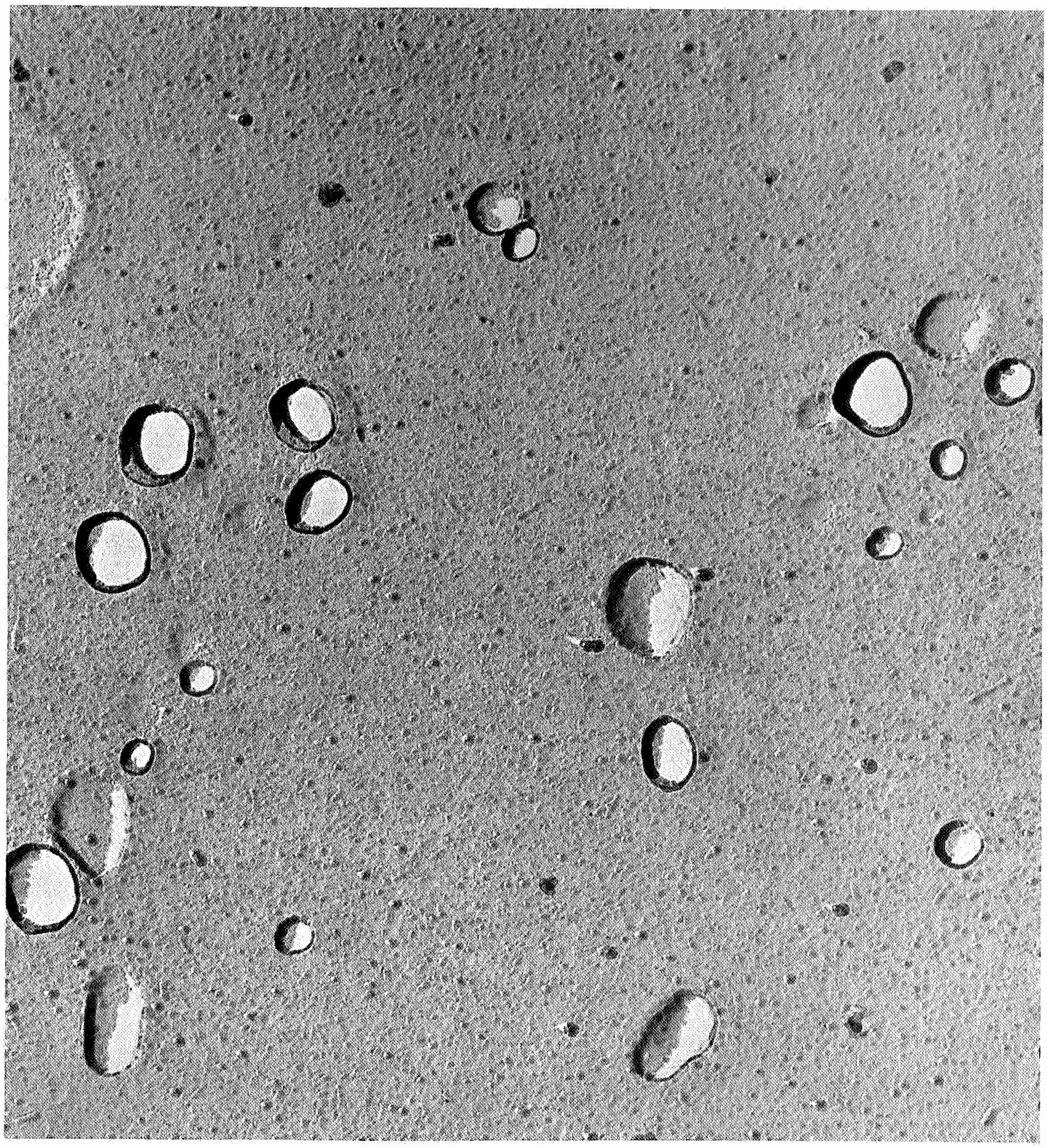
1000X 1D421

FIGURE NO. 15. STABILITY OF DISPERSION IN CHROMIUM-Th02 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)



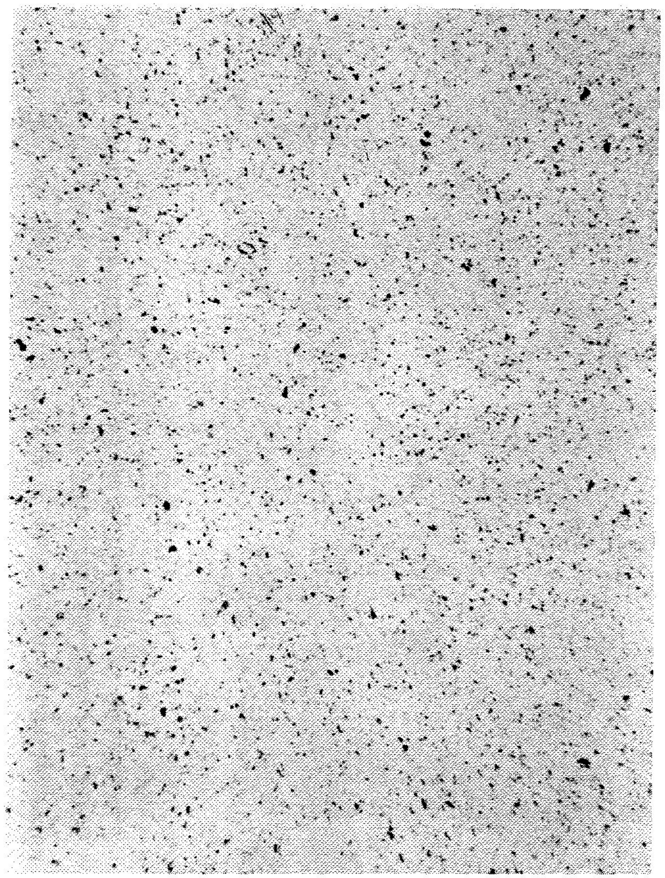
10,000X $\underline{1\mu}$ EH-1333

FIGURE NO. 15A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)

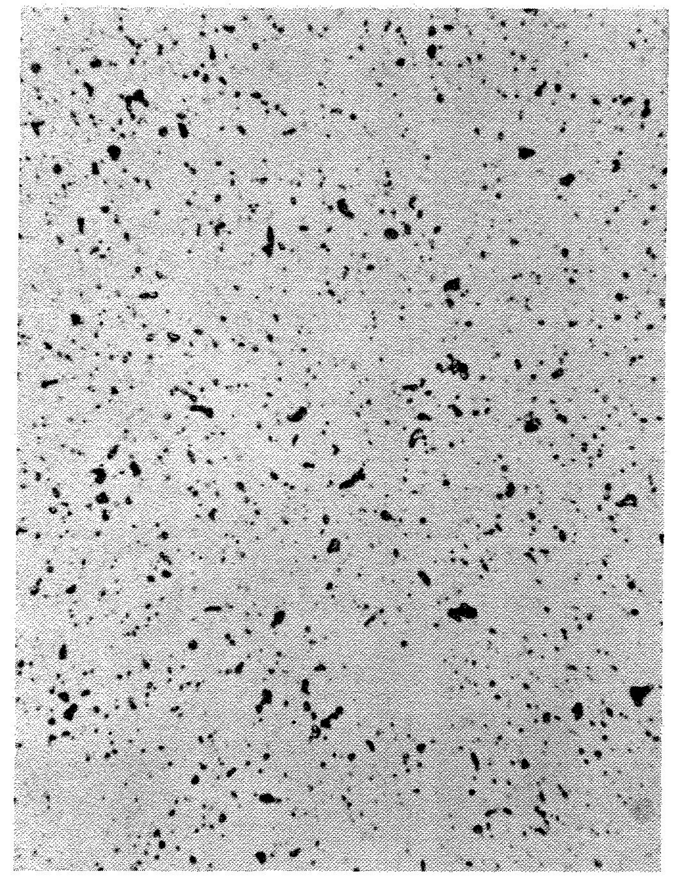


50,000X 1μ EH-1334

FIGURE NO. 15B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-38-11, 2.0 vol % ThO_2, Pellet No. 11-2)

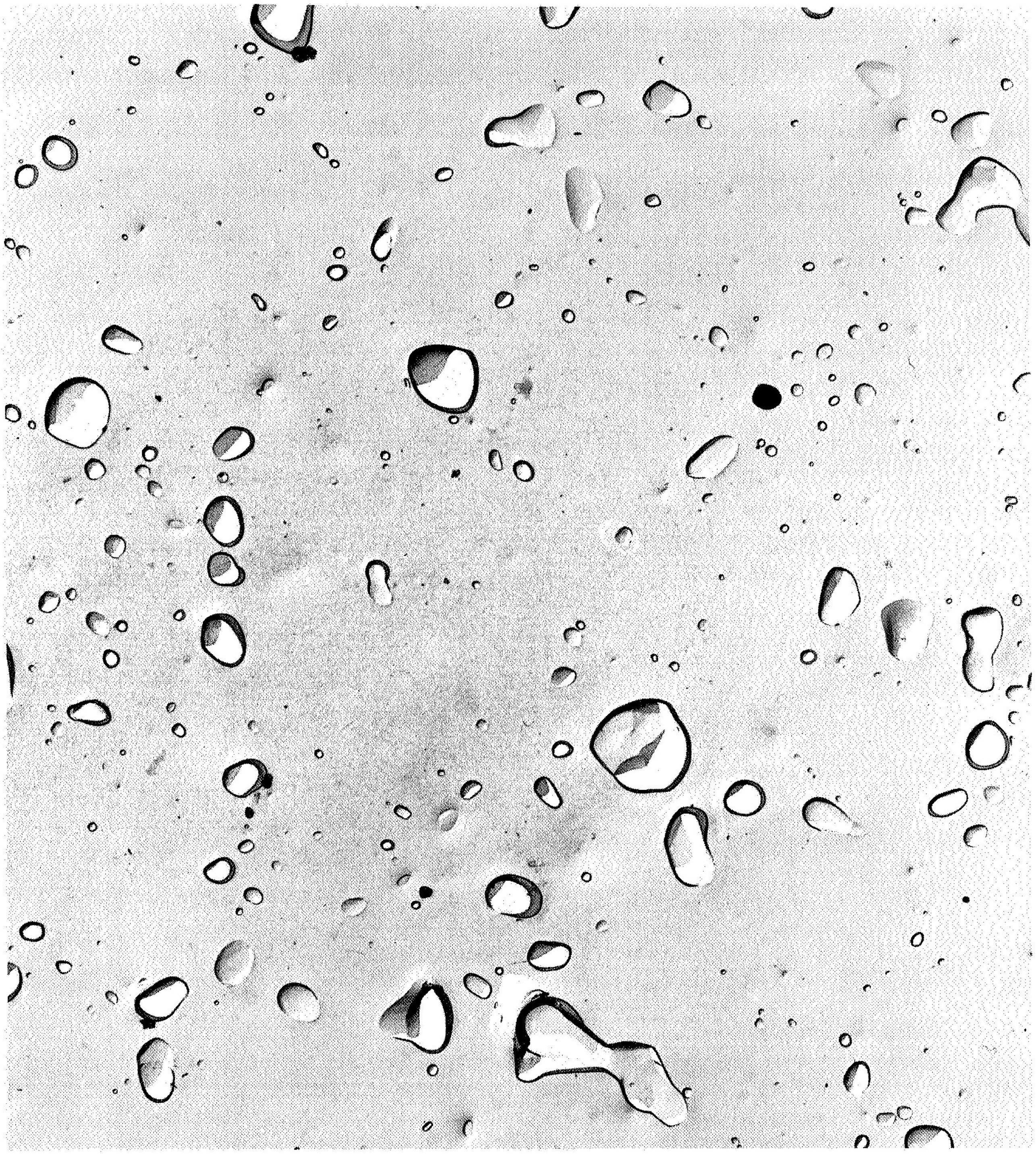


250X 1D417



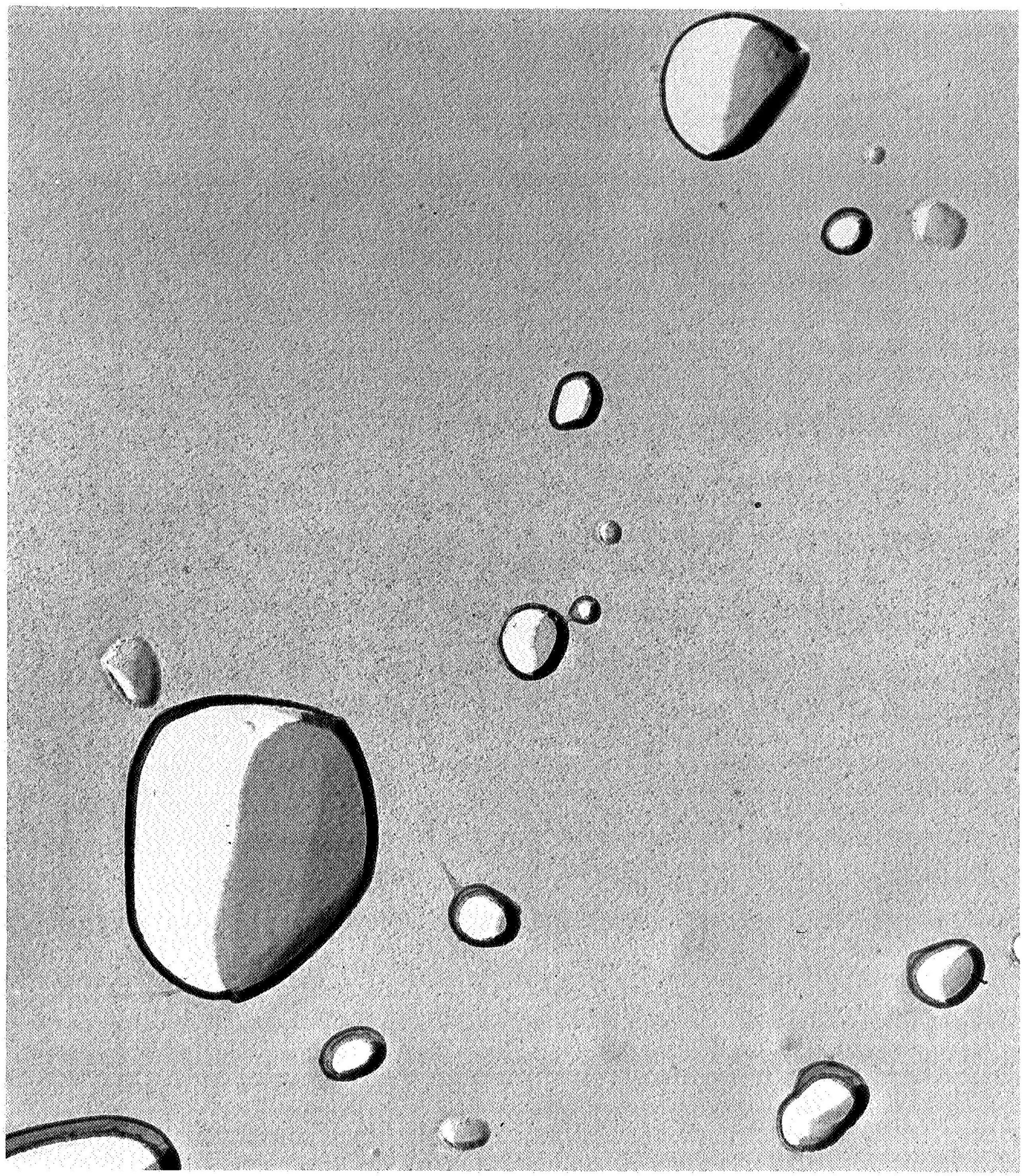
1000X 1D422

FIGURE NO. 16. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)



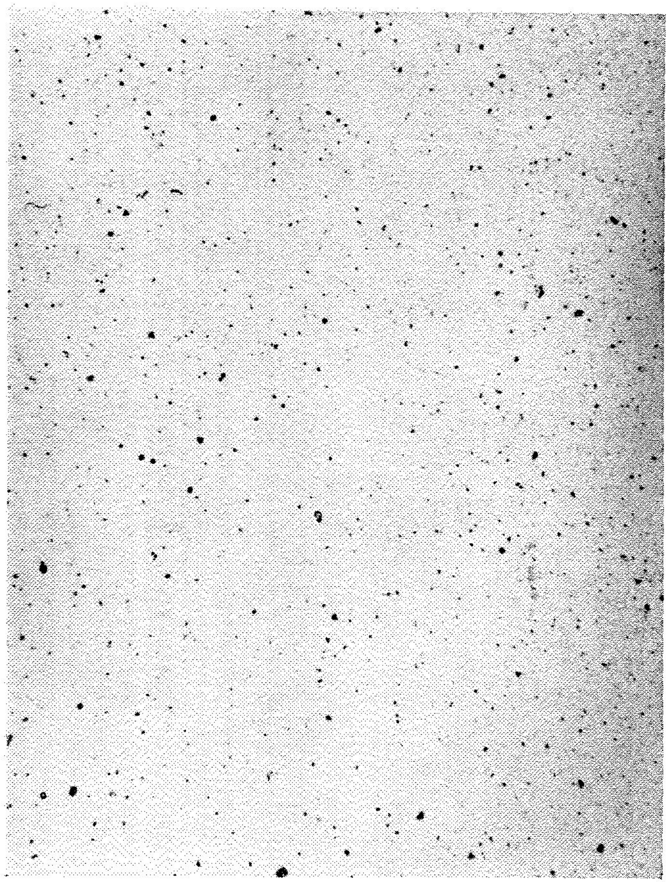
10,000X $\quad$ 1μ $\quad$ EH-1331

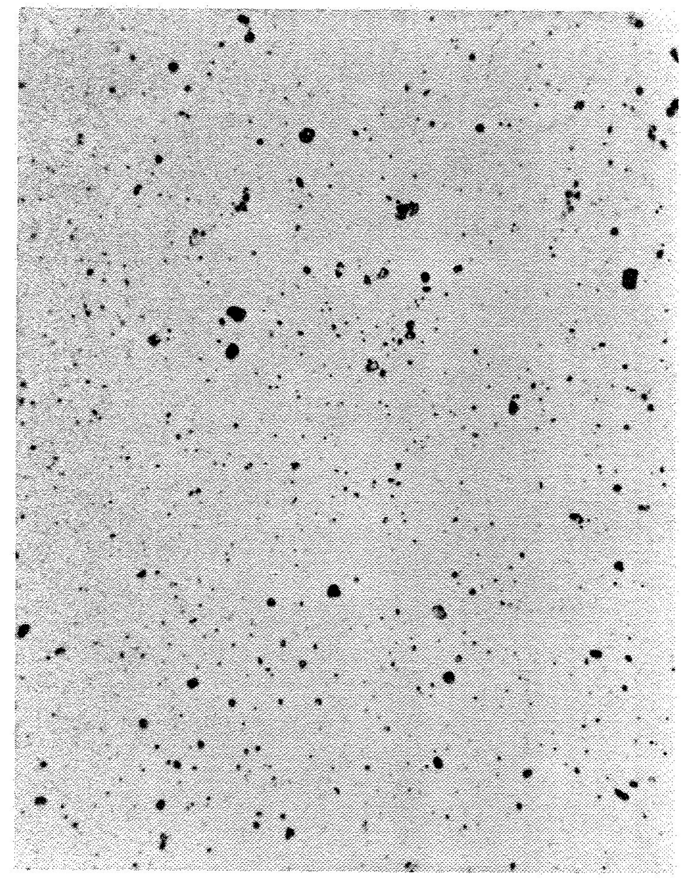
FIGURE NO. 16A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)



50,000X | 1μ | EH-1332

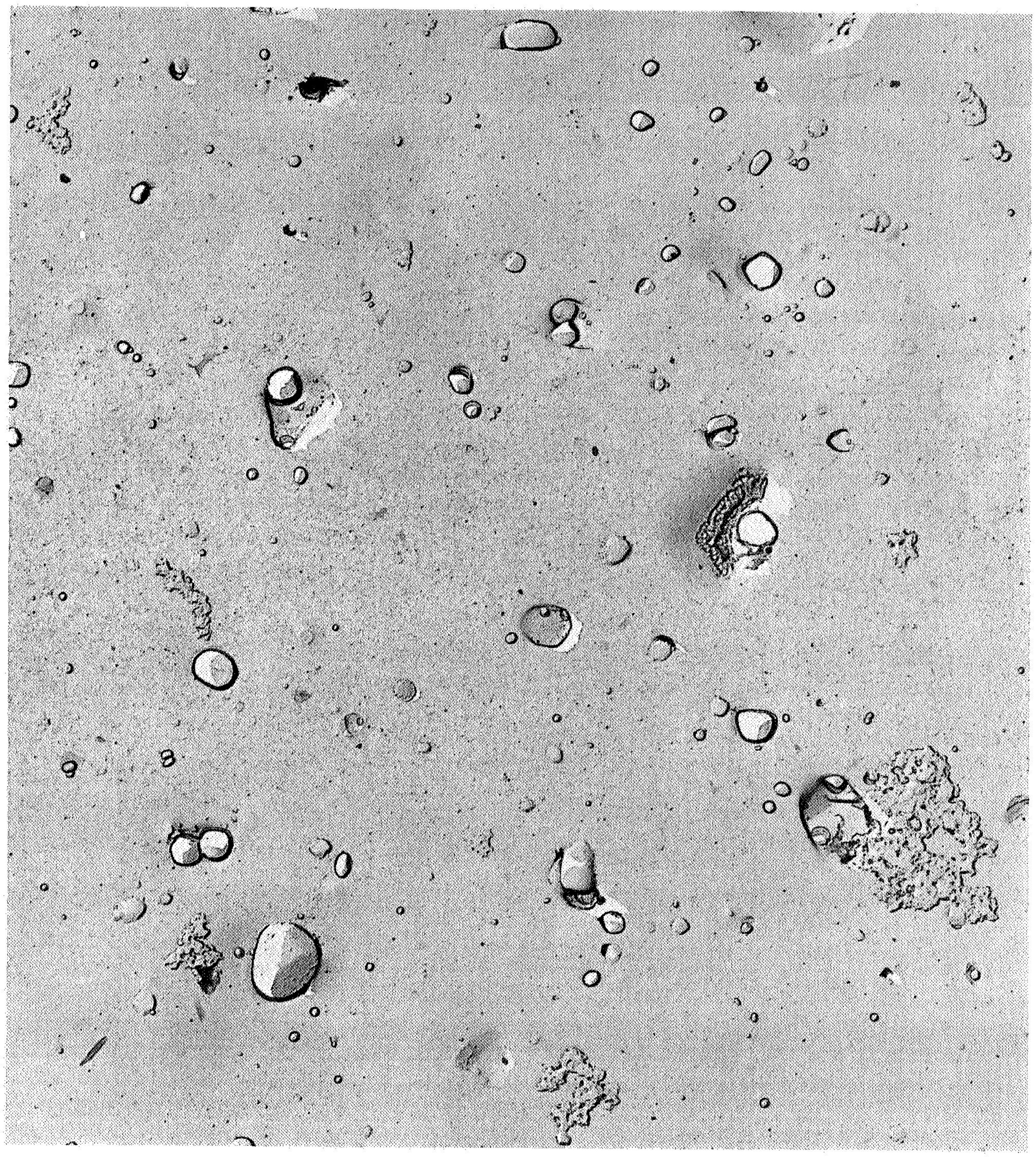
FIGURE NO. 16B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-41-12, 5.0 vol % ThO_2, Pellet No. 12-2)





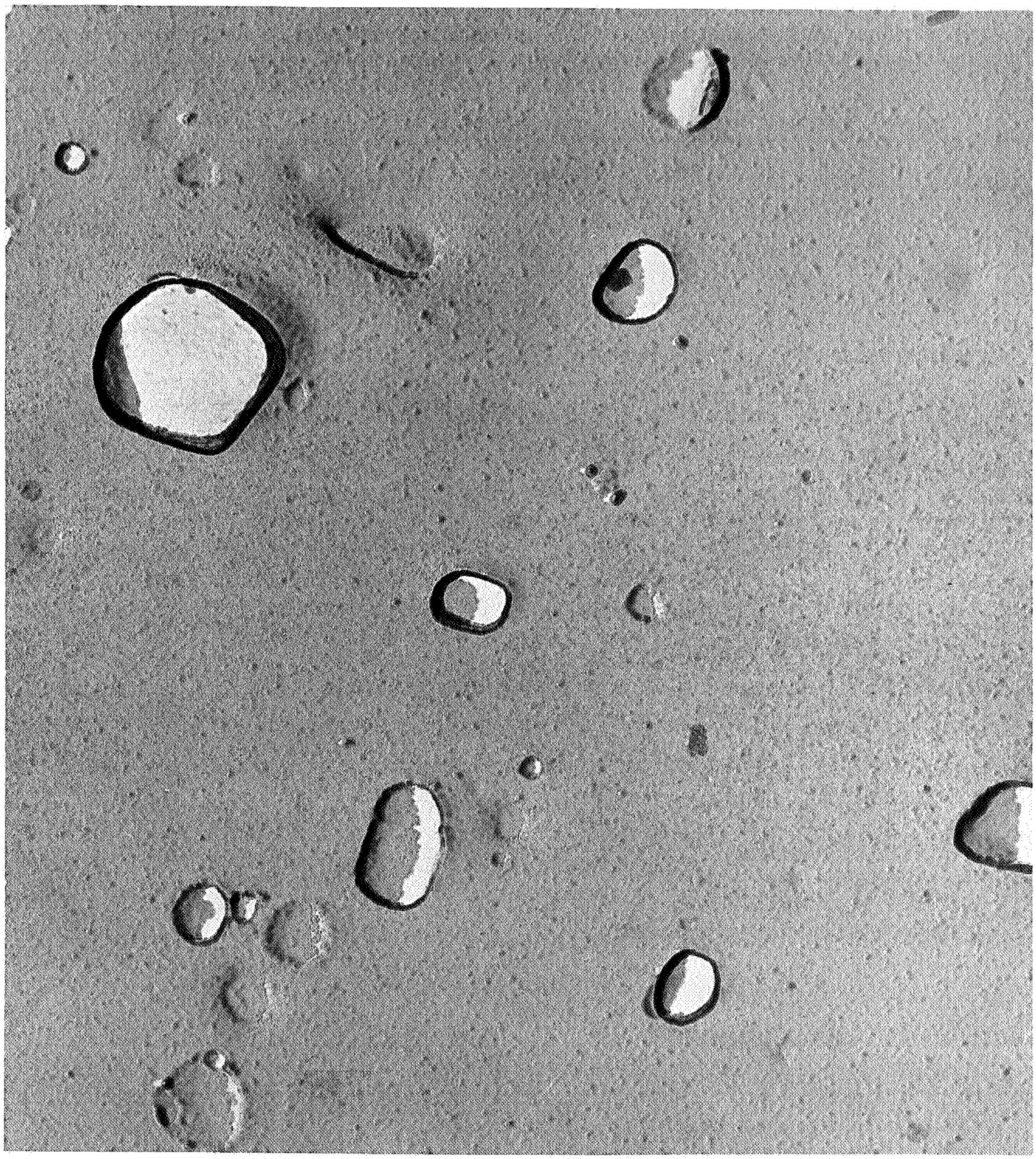
250X 1D420 1000X 1D425

FIGURE NO. 17. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)



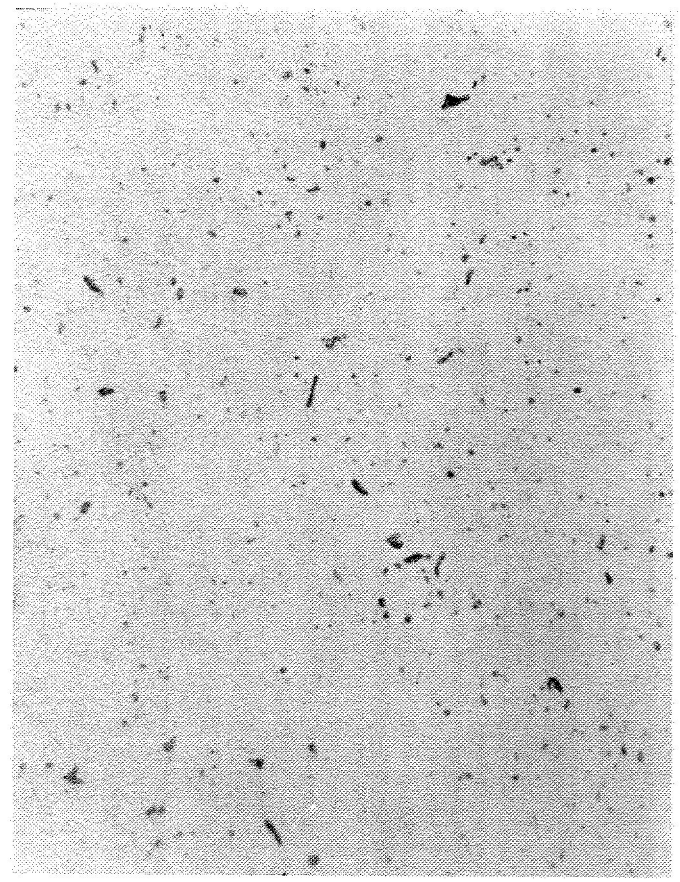
10,000X 1μ EH-1335

FIGURE NO. 17A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)



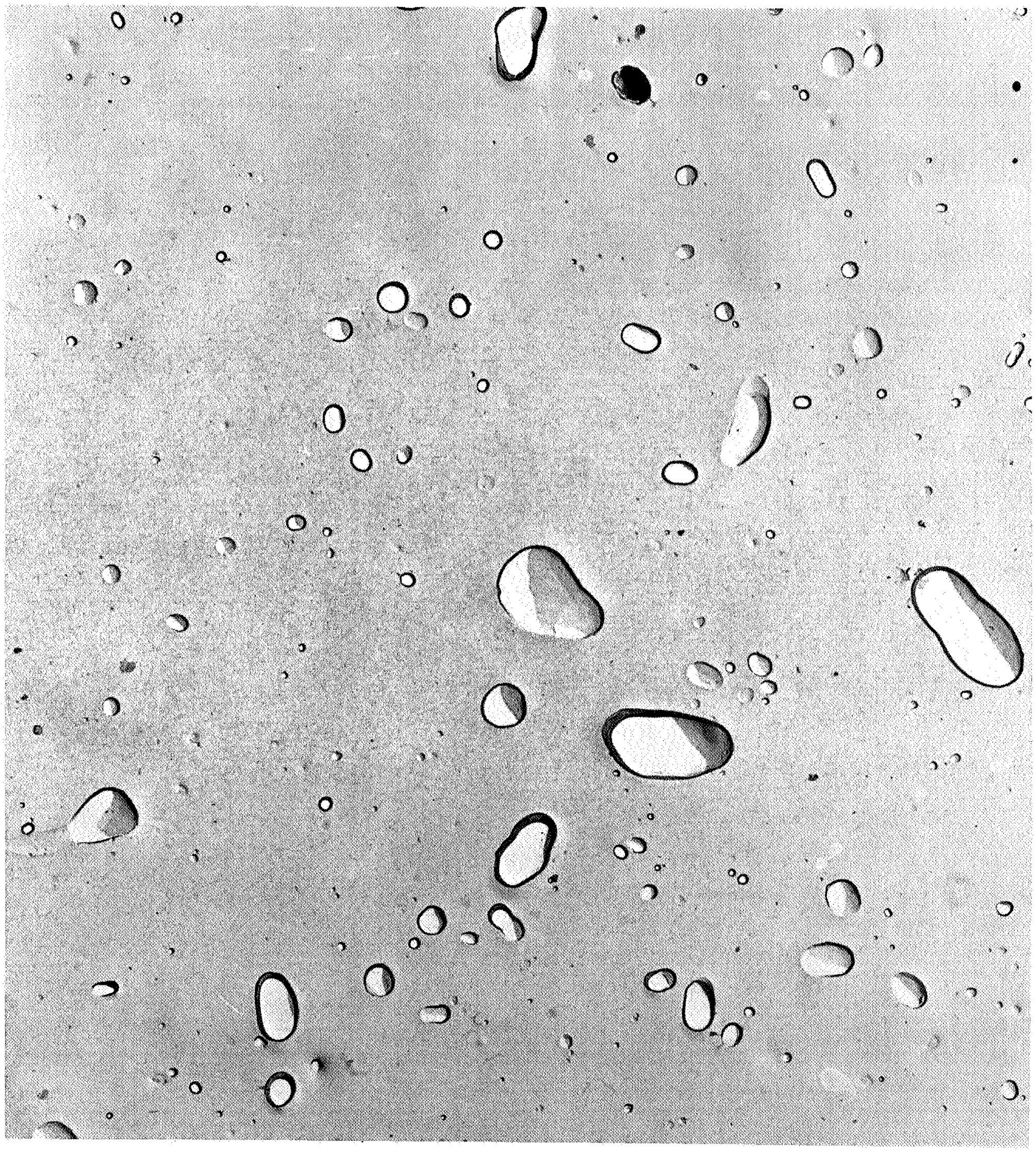
50,000X 1μ EH-1336

FIGURE NO. 17B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-52-16, 2.9 vol % ThO_2, Pellet No. 16-1)



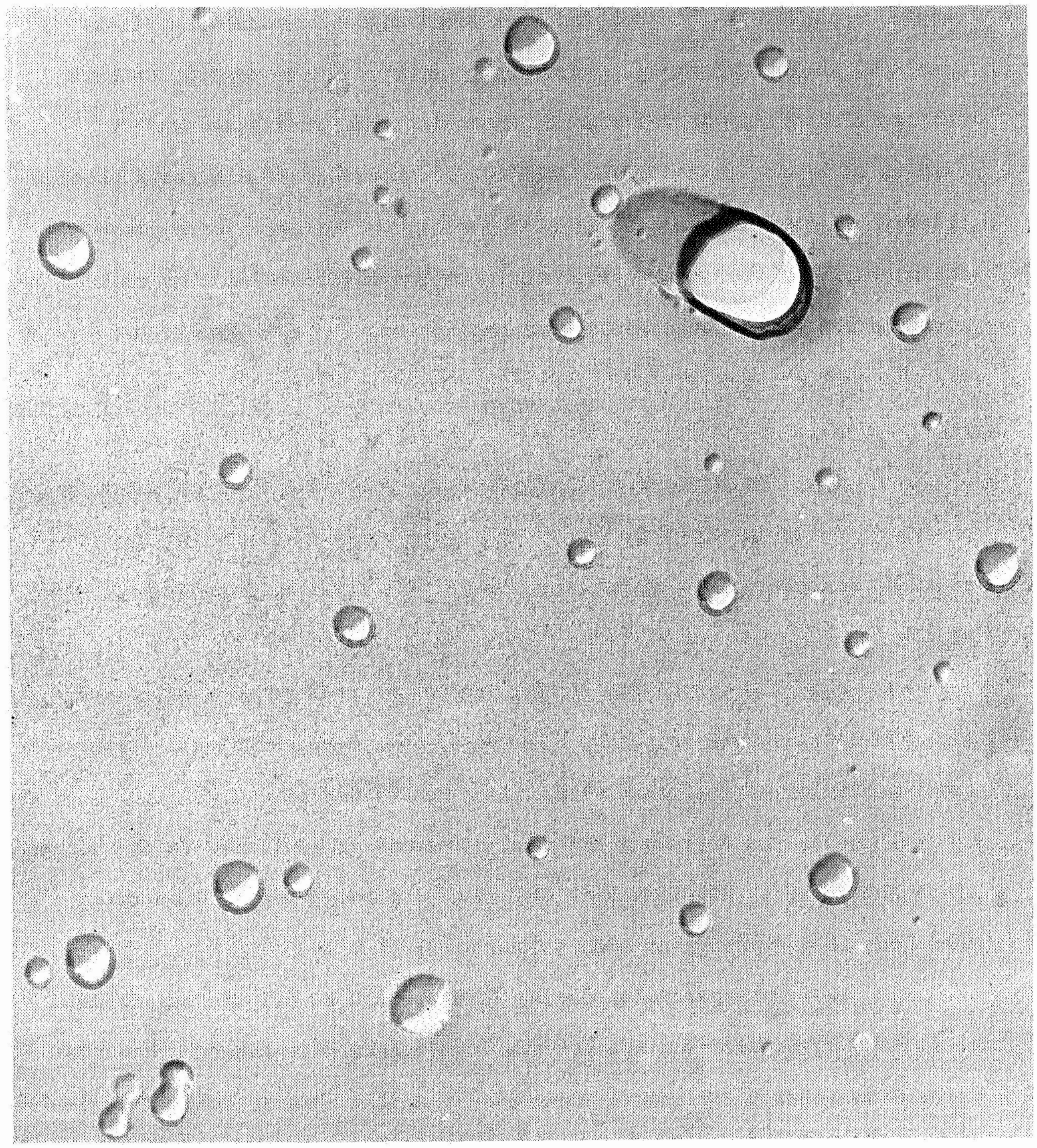
250X 3D409 1000X 3D412

FIGURE NO. 18. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-2)



10,000X — 1μ — EH-1486

FIGURE NO. 18A. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-2)



50,000X $\quad$ 1μ $\quad$ EH-1487

FIGURE NO. 18B. STABILITY OF DISPERSION IN CHROMIUM-ThO_2 HEAT TREATED AT 2600 F (1700 K) FOR 100 HR. (Powder Preparation No. 24991-71-24, 2.0 vol % ThO_2, Pellet No. 24-2)

lineal analysis, summarized in Table 6, do not indicate a significant change in the IPS as a result of heat treatment. Consequently, it is concluded that, even though coalescense occurs if ThO_2 to ThO_2 contact exists, the particles that are not in contact do not migrate and the dispersion is considered to be stable. A comparison of Figures 8 through 11B with Figures 12 through 18B also indicates that pores were closed during the heat treatment. Therefore, it can be concluded that objectionable gas-pocket microvoids were not formed.

CONCLUSIONS

(1) The process developed for the preparation of chromium-ThO_2 powder is suitable for preparation of a pure-metal matrix with concentrations of dispersed ThO_2 within about ± 0.5 vol % of the intended composition.

(2) The capability of the process to produce an ideal dispersion has not been demonstrated. Clumps of ThO_2, along with well-dispersed small particles of ThO_2, are obtained on consolidation.

(3) The frequency and size of clumps is sensitive to the method of consolidation. Hot isostatic pressing produces a better dispersion than does cold pressing at high pressure.

(4) Interparticle spacing (IPS) of 3.0 to 5.1 microns (3.0×10^{-6} to 5.1×10^{-6} m) obtained in the present investigation is greater than the desired IPS of 1.5 microns (1.5×10^{-6} m). Use of a more suitable ThO_2-feed material and reduction by extrusion and/or rolling after hot isostatic pressing may be beneficial.

TABLE 6. INTERPARTICLE SPACING IN CONSOLIDATED CHROMIUM-ThO_2

Run No.	ThO_2 Conc, vol %	Pellet No.	Interparticle Spacing, μ (10^{-6} m)		
			As-Consolidated	After Heat Treating for 100 Hr	
				2400 F (1590 K)	2600 F (1700 K)
24991-38-11	2.0	11-1	-	3.0	-
		11-2	4.2	-	4.5
24991-41-12	5.0	12-2	3.5	-	3.3
		12-3	-	4.6	-
24991-52-16	2.9	16-1	5.1	-	4.0
24991-71-24	2.0	24-1	3.2	-	-
		24-2	-	-	4.7
		24-3	-	4.5	-

(5) The dispersion of ThO_2 in a pure-chromium matrix is stable at 2600 F (1700 K) with respect to movement of individual particles. However, individual particles and clumps of particles are spheroidized during heat treatment.

(6) The hardness of the chromium-ThO_2 does not appear to be increased during high-temperature heat treatment. In fact, the hardness of five out of seven specimens decreased. Grain growth and stress relief are suspected causes of the observed decrease in hardness.

RECOMMENDATIONS

In view of the facts that (1) a fair dispersion of controlled ThO_2 concentrations can be obtained, (2) a high-purity-chromium matrix is formed, and (3) the dispersions are stable for extended periods of time at elevated temperatures, it is recommended that the development of dispersion-strengthened chromium prepared by vapor deposition of iodide chromium be continued. The continuation of the development should include scale-up of the process to the extent that one-pound quantities of the chromium-ThO_2 powder can be prepared and consolidated to provide material for fabrication studies and mechanical-property measurements. Improvement in the interparticle spacing of ThO_2 by process modifications and/or by fabrication procedures should be considered. At present, scale-up of the process beyond that required to provide material for mechanical-property measurement is unwarranted.

It is recommended that the scale-up of the iodide process be done in such a way as to be compatible with substitution of hydrogen reduction of the chloride in a few experiments. In this way, the feasibility of preparing an equivalent but potentially cheaper product from the chloride could be assessed.

APPENDIX

DESIGN OF THE CHROMIUM ThO_2 PREPARATION UNIT

Discussion

At the start of the investigation, it was known from previous experience that CrI_2 could be efficiently reduced with hydrogen. It was also known from previous experience that a continuous feed of 12x60-mesh ($1.68 \times 10^{-3} \times 2.5 \times 10^{-4}$m) particles of CrI_2 could be satisfactorily controlled at feed rates of 5 grams per hour (1.35×10^{-6}kg/s) or more. However, with the size of apparatus planned for the present investigation, some development work was required for feeding submicron ThO_2 as individual particles at rates of less than one gram per hour (2.78×10^{-7}kg/s). The collection of a submicron product without contamination by exposure of the powder also required development. The finalized design of the apparatus is shown in Figures A-1 through A-6, and the various components are discussed in the following sections.

ThO_2 Feeder

Based on a predetermined chromium-formation rate of 15 to 20 grams per hour (4.6×10^{-6} to 5.55×10^{-6}kg/s), the rate of ThO_2 feed required to yield 2 vol % ThO_2 in the chromium is 0.42 to 0.56 grams per hour (1.17×10^{-7} to 1.56×10^{-7}kg/s). To achieve a continuous feed of the submicron ThO_2, three feeder designs were tried and two were judged to be unsatisfactory. Initially, a feeder similar to the one used for CrI_2 (see Figure A-2) was used. With the feeder, a motor drive raises the ThO_2 charge and vibration, applied to the feeder, causes particles to fall into a stationary central tube connected to the coating unit. The

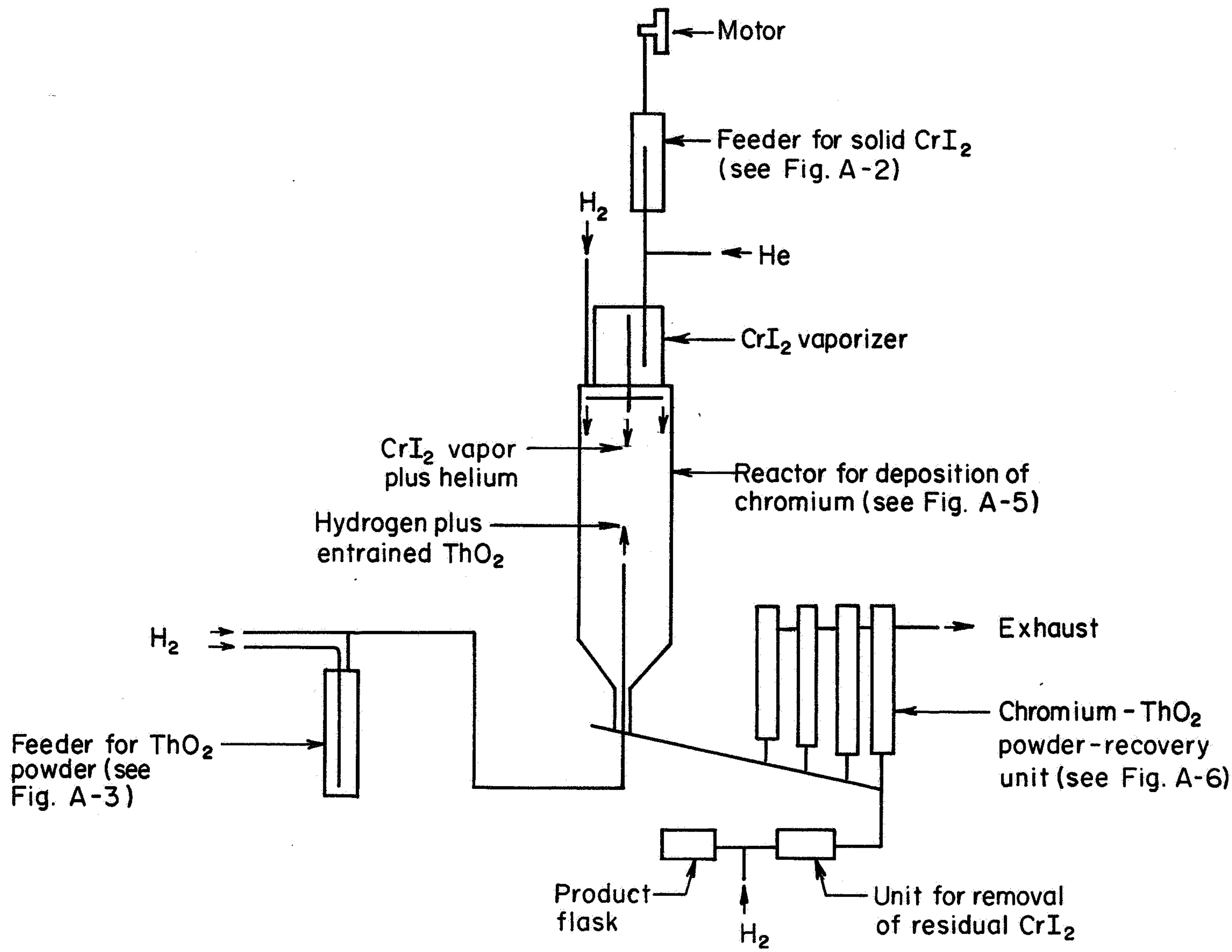


FIGURE A-1. APPARATUS FOR THE PREPARATION OF CHROMIUM-ThO_2 POWDER

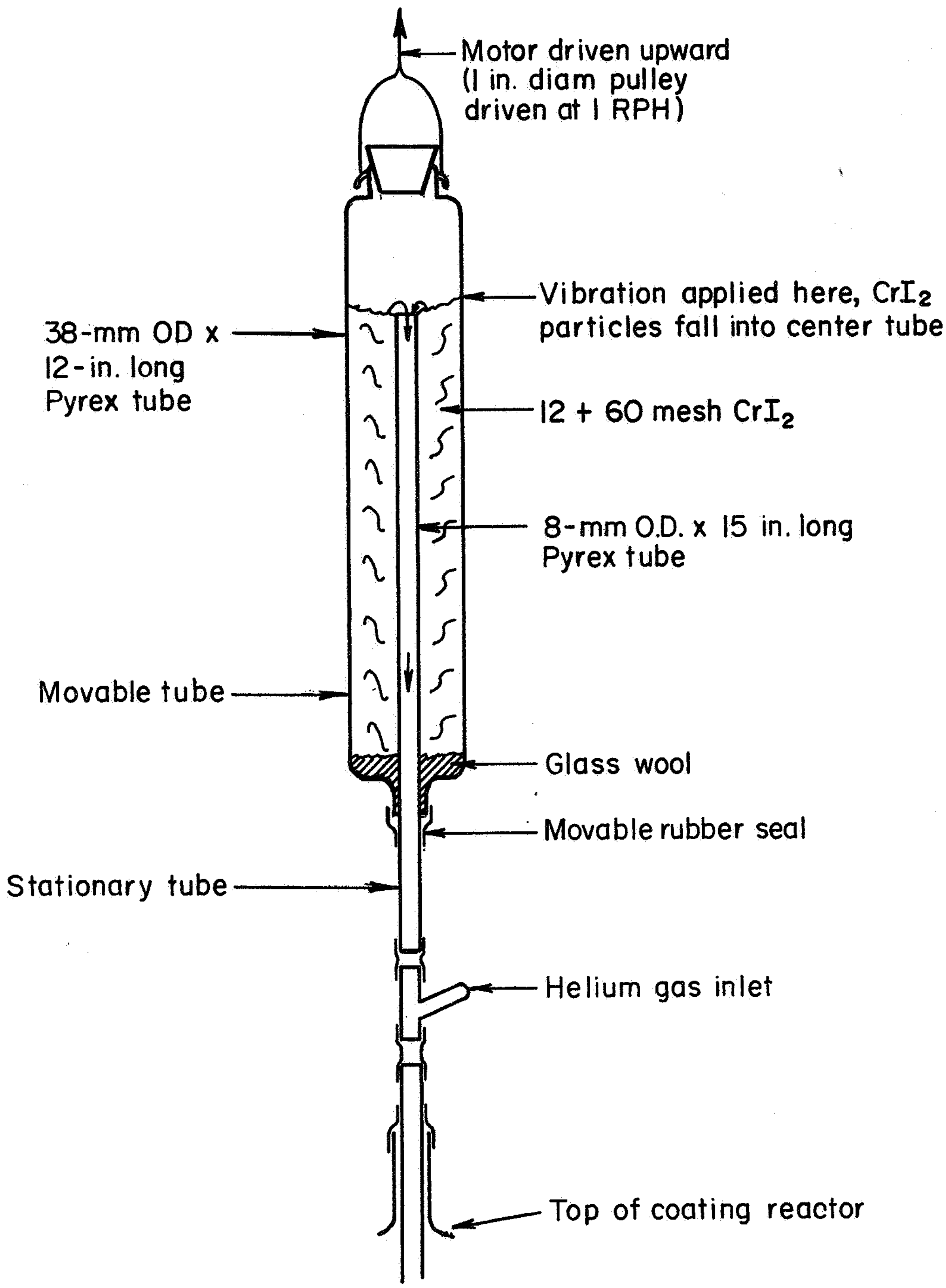


FIGURE A-2. SOLID CrI_2 FEEDER ASSEMBLY

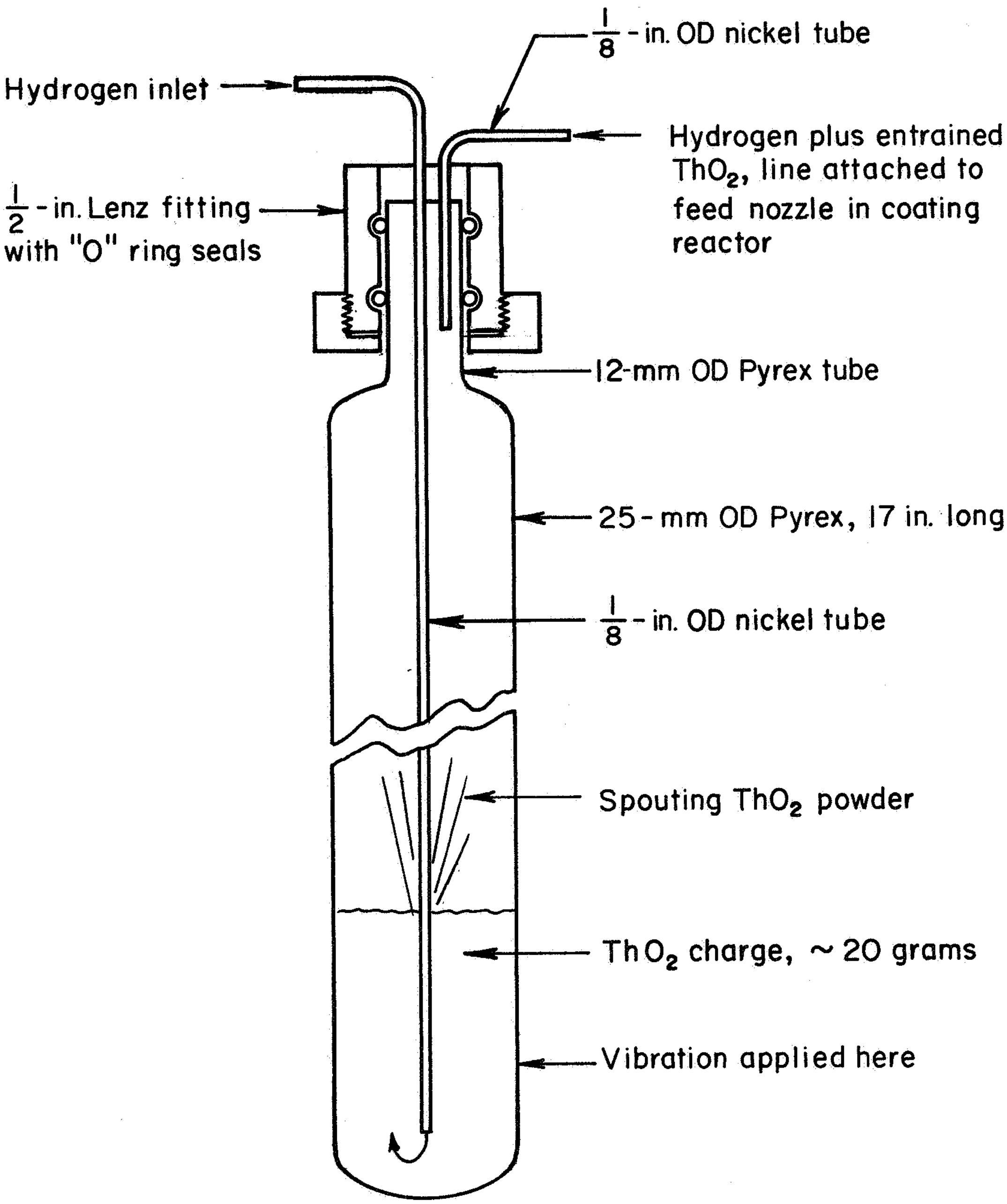


FIGURE NO. A-3. THORIA FEEDER

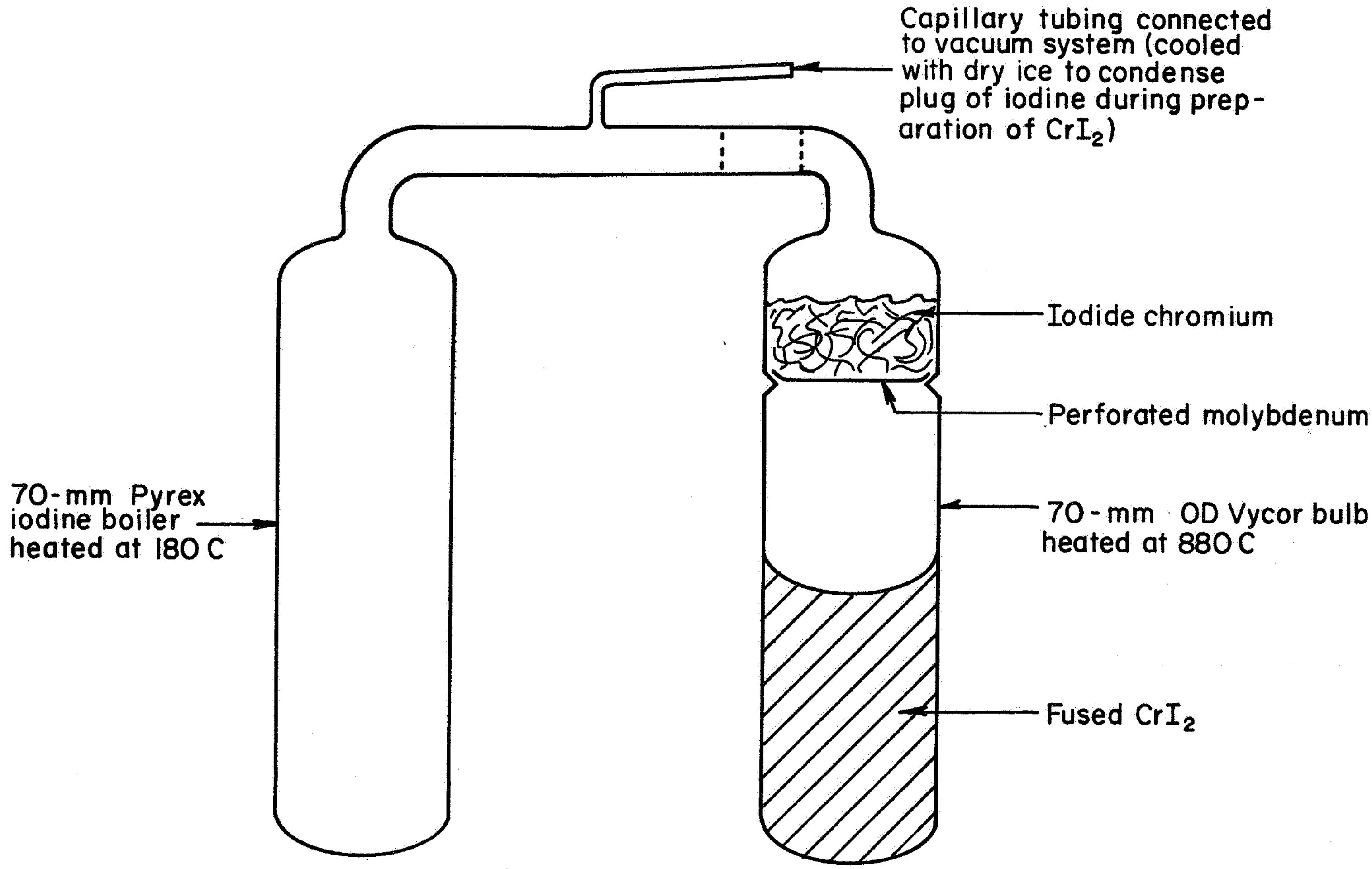


FIGURE A-4. APPARATUS FOR PREPARATION OF CHROMOUS IODIDE

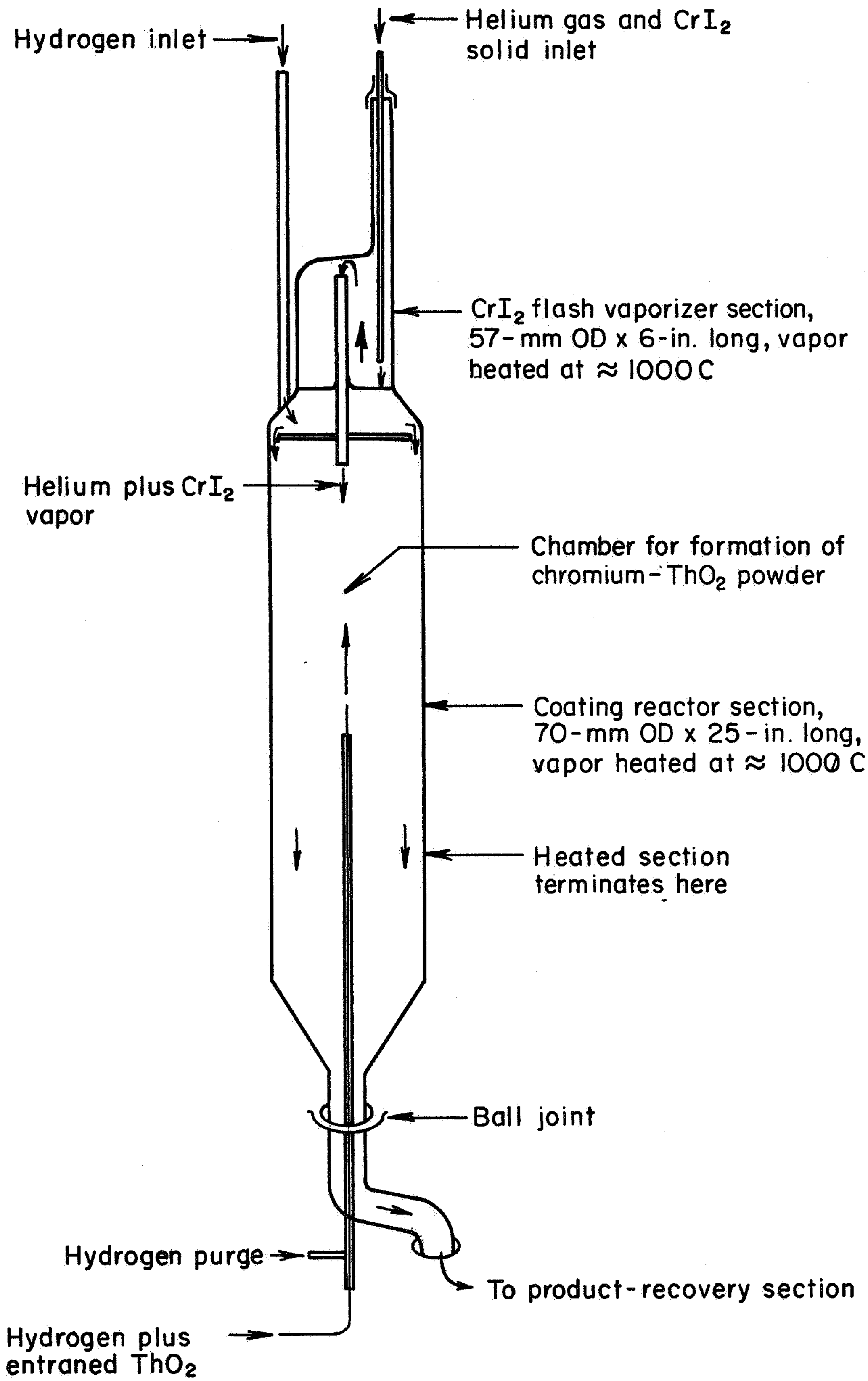


FIGURE A-5. REACTOR FOR DEPOSITION OF CHROMIUM-ThO_2 POWDER

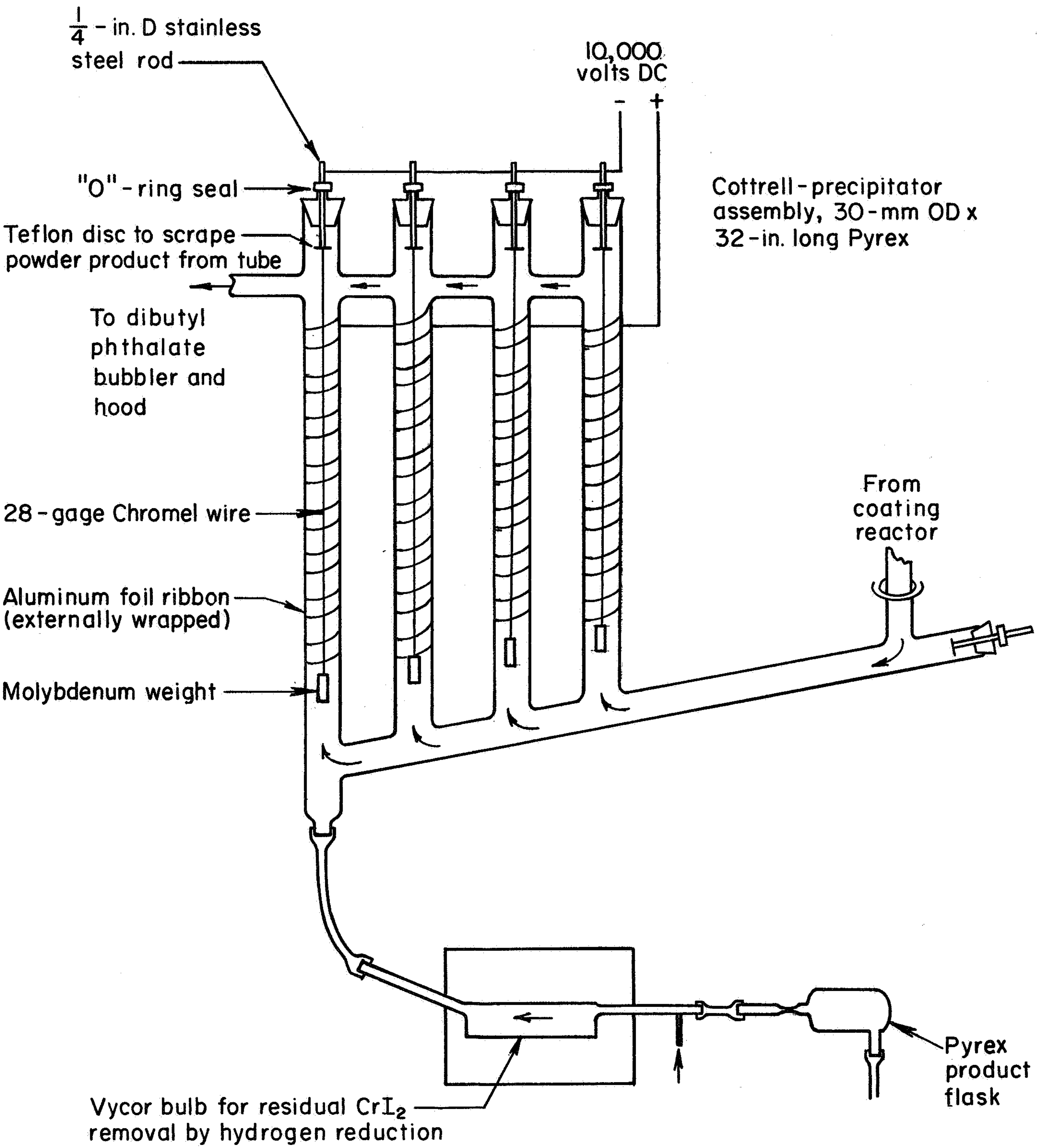


FIGURE A-6. CHROMIUM-ThO_2 POWDER-RECOVERY APPARATUS

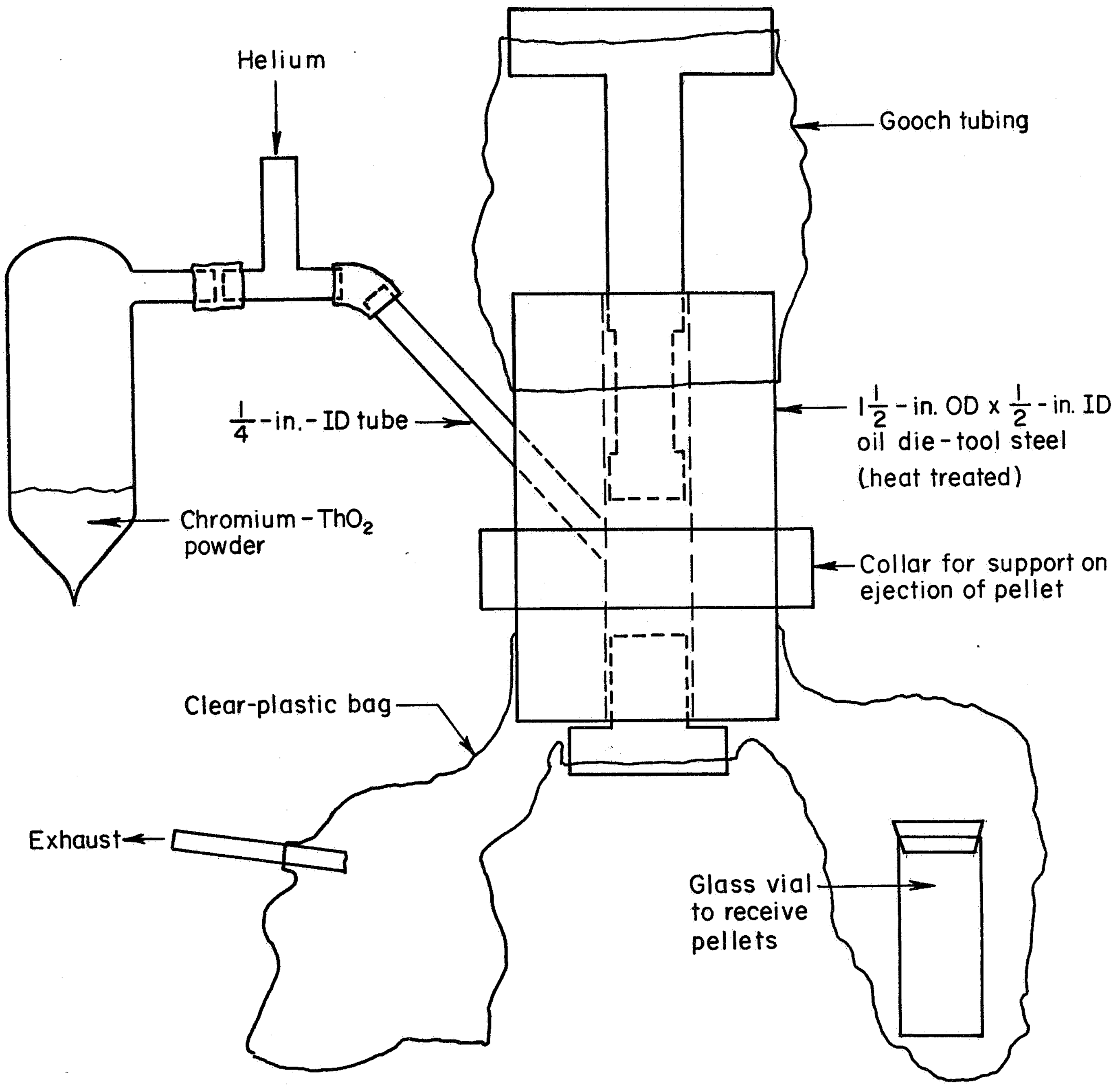


FIGURE A-7. ASSEMBLY FOR COLD-PRESSING CHROMIUM-ThO_2 POWDER

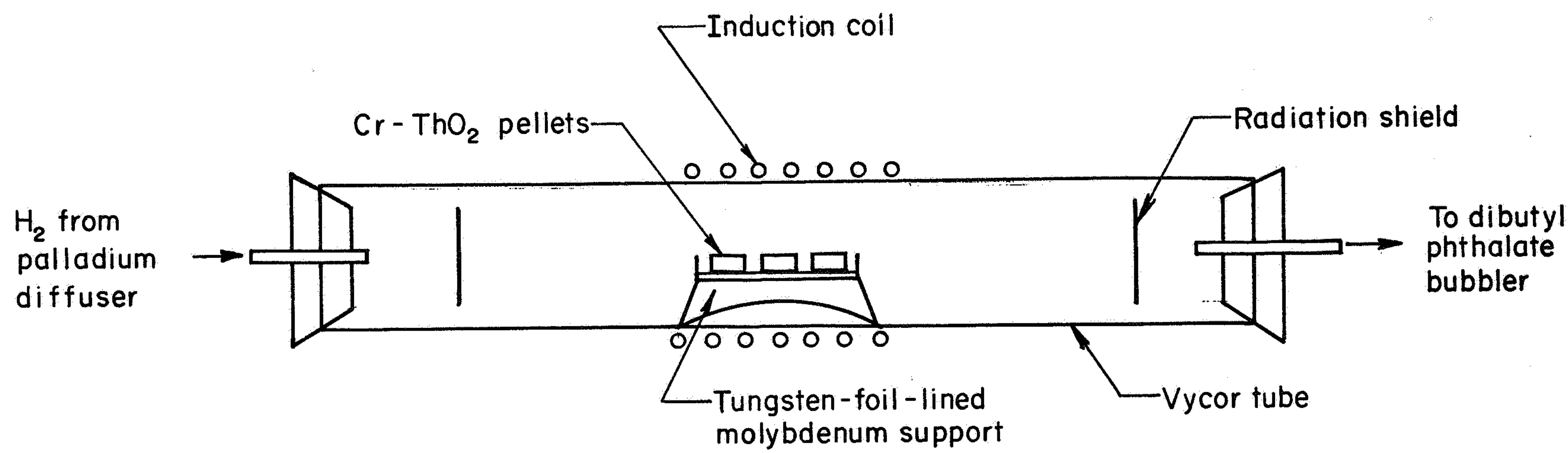


FIGURE A-8. ASSEMBLY FOR SINTERING Cr-ThO_2 PELLETS IN HYDROGEN performance was found to be unsatisfactory for feeding submicron ThO_2, since the charge settled at an uncontrolled rate which resulted in a variable feed rate. In an attempt to circumvent the problem, the feeder was modified. A disc with four 1/16-in. (1.52×10^{-3} m)-wide slots cut into the periphery was mounted on the central stationary tube of the feeder so that ThO_2 could be compacted prior to a run. The ThO_2 container was oscillated in addition to being moved upward, with the result that ThO_2 was continuously scraped against the disc to force ThO_2 through the slots and thereby control the amount dropped into the stationary control tube. The oscillating design was an improvement over the initial design, but variations in the amount of precompaction plus random changes in the compact with vibration caused uncontrolled variations in feed rate.

The feeder shown in Figure A-3 was evaluated and found to be satisfactory. Gas is forced through a charge of ThO_2 to entrain particles, while vibration is applied to prevent channeling. The rate of feed is controlled by the rate of gas flow through the charge. For example, feed rates of about 0.4, 0.5, and 0.8 gram per hour (1.11×10^{-7}, 1.39×10^{-7}, and 2.22×10^{-7} kg/s) are obtained with hydrogen flow rates of 0.75, 1.00, and 1.30 liters per minute (1.25×10^{-5}, 1.67×10^{-5}, and 2.17×10^{-5} m^3/s), respectively. Initial feed rates obtained with a new charge of ThO_2 are usually twice those reported above, but decrease to the reported values during operation over a time period of about four hours with 20 to 30 grams (2.0×10^{-2} to 3.0×10^{-2} kg) of ThO_2 charged to the feeder. Consequently, preconditioning of a new charge is a recommended procedure.

ThO_2 Injector

In order to minimize the injection of agglomerates into the coating chamber, the entrained ThO_2 was blown through a small-bore tube (47-mil IDx24-in. in length) (1.19×10^{-3}m IDx6.1×10^{-1}m), as indicated in Figure A-1. Although smaller bore tubes should be more effective, the smaller bores limit the gas flow necessary for entrainment and are prone to becoming plugged with ThO_2 agglomerates at the inlet end. Consequently, the 47-mil (1.19×10^{-3}m)-ID tube was selected as a workable size.

Electron microscopic examination of collected samples of Linde "B" smoke (0.03-μ diameter), ejected from a 16-mil (4.06×10^{-4}m) ID by 2-in. (5.08×10^{-2}m) long tube at a velocity of about 820 foot per second (250m/s), indicated that at least 80 percent of the smoke collected was of single particles. Although the effectiveness would decrease with the increase in diameter from 16 to 47 mils (4.06×10^{-4} to 1.19×10^{-3}m), the loss in effectiveness was at least partially offset by the extension of the length from the 2 inches (5.08×10^{-2}m) used for the evaluation to the 24 inches (6.1×10^{-1}m) used in the coating unit. Samples of ThO_2 smoke were not collected external to the coating unit because of health hazard.

CrI_2-Feed System

In order to insure a continuous and controlled rate of feed for the CrI_2, the assembly shown in Figure A-2 was chosen. The CrI_2 was prepared as an ingot in five to six-pound lots (2.27 to 2.72 kg) in the apparatus shown in Figure A-4 by iodination of iodide chromium. The ingots of CrI_2 were crushed to 12x60 mesh (1.68×10^{-3}x2.50×10^{-4}m) particles in a helium-filled dry box and loaded into the mechanical feeder. Although slight variations of feed rate of CrI_2 to the vaporizer section can occur, the average feed rates for the preparation runs were reproducible to about ± 10 percent of the average. The slight variations are leveled out by operation of the vaporizer section under constant conditions of temperature and carrier gas flow rate which allows accumulation of an overfeed in the vaporizer section. The accumulation resulting from the overfeed is evaporated during periods of underfeeding. The combination of a mechanical feed to a vaporizer avoids variations in feed rate obtained with the often used method of passing a carrier gas continuously over a large charge of liquid CrI_2. In the latter type system, the feed rate may vary considerably as a result of thermal dissociation of CrI_2 which forms a crust of chromium on the surface of the liquid. Another method, which involves a controlled feed of iodine through a bed of chromium and transport of the iodination product (CrI_2) to the coating chamber, was ruled out as being less convenient than the solid CrI_2-feed system. However, for scale-up of the preparation apparatus, the combined iodination and transport method is favored.

Coating-Reaction Chamber

The reaction-chamber design used for most of the chromium-ThO_2 powder preparations is shown in Figure A-5. The flow of hydrogen passed a quartz plate and directed downward along the wall of the chamber was incorporated with the intent to minimize formation of dense chromium on the walls of the chamber. However, it was observed that deflection of the CrI_2-helium mixture by chromium deposition on the nozzle negated the potential advantage of the approach. Injection of ThO_2 entrained in hydrogen countercurrent to the flow of the He-CrI_2 mixture and the hydrogen along the wall should result in a larger dwell time for the ThO_2 in the coating region than would be obtained by concentric injection from the top of the unit.

Although the period of time that the unit can be operated is limited to about four hours as a result of chromium deposition and blockage of the He-CrI_2 inlet, the design is suitable for preparation of limited quantities of material. Determination of the optimum design for product yield was considered to be beyond the scope of the present investigation, which was to demonstrate the feasibility of preparing a dispersion-strengthened product. Consequently, the design was essentially limited to one that was found to yield a product of interest early in the present investigation.

Collection of Powder Product

The unit designed for collection of the powder product by electrostatic precipitation is shown in Figure A-6. With a total gas flow of 25 to 30 liters per minute ($4.17\text{x}10^{-4}$ to $5.0\text{x}10^{-4}\text{m}^3/\text{s}$) and a potential of 8 to 10 thousand volts, the loss of material by incomplete disentrainment was limited to about 10 percent. At the conclusion of a powder-preparation run, the gas flows were decreased to about 1 liter per minute ($1.67\text{x}10^{-5}\text{m}^3/\text{s}$), the high-voltage source was disconnected, and the walls of the collection unit were scraped with the built-in Teflon scrapers. The powder was pushed into a Vycor bulb, shown in Figure A-6, and heated in hydrogen at 1470 F (1070 K) for four hours to remove residual CrI_2 by evaporation and/or reduction. The cleaned powder was then transferred to a product flask, shown in Figure A-6, by tilting the assembly to a near-vertical position. The product flask was then sealed by fusion to insure that the powder would not be contaminated on storage.

Cold Pressing the Chromium-ThO_2 Powder

A small steel die, shown in Figure A-7, was designed for connection to the product flask. The die assembly was purged with helium and then the purge line was closed with a hose clamp. An estimated weight of chromium-ThO_2 powder was poured from the product flask into the die and then pressed at 30,000 psi ($2.07 \times 10^8 N/m^2$). The pellet was ejected into the attached helium-filled bag and then placed in an ampoule contained in the bag. The pressing operation was repeated until all of the chromium-ThO_2 powder was converted to pellets. The pellets were either canned for hot isostatic pressing or given a second hydrogen heat treatment at 2370 F (1570 K) for three hours to insure that the product would be low in the contaminant Cr_2O_3. The apparatus used for the high-temperature hydrogen heat treatment is shown in Figure A-8.

Purification of Hydrogen and Helium

Both helium and hydrogen were purified by methods that had been demonstrated to be effective in previous work with metal coatings at BCL. The hydrogen was purified with a commercially available unit which diffuses the hydrogen through palladium-silver alloy tubes. Since the impurities

H_2O, CO, CO_2, CH_4, N_2, etc, do not diffuse through the palladium, the hydrogen is effectively purified.

Since it does not diffuse through palladium, another method of purifying helium is required. A zirconium-sponge getter heated at 1380 to 1560 F (1020 to 1120 K) is effective, provided that the unit is made sufficiently large. A 4-inch ID by 37-inch (1.02×10^{-1} m IDx0.94) long stainless steel tube with a 24-inch (0.61 m) long heated zone filled with zirconium sponge is sufficient for purification of about 20 liters per minute ($3.33 \times 10^{-4} m^3/s$) of helium.

<u>Procedure for the Preparation of Chromium-ThO_2 Powder</u>

The apparatus is assembled as shown in Figures A-1 through A-6. The CrI_2 and the ThO_2 are charged to the feeders in a helium-filled dry box prior to attachment to the preparation unit. All gas lines connected to the unit are evacuated and then filled with the desired gas to eliminate pockets of air accumulated between preparations. The CrI_2 feeder is purged for one hour at a helium flow rate of about two liters per minute ($3.34 \times 10^{-5} m^3/s$) by inserting a wire to cause leakage between the rubber seal and the central stationary tube of the feeder. The flexible line connection to the vaporizer section is clamped shut so that helium is forced in through the charge of CrI_2. All other sections of the apparatus are then purged for several hours. The ThO_2 feeder is purged at a flow rate of 0.1 liters per minute ($1.67 \times 10^{-6} m^3/s$). At the low flow rate, the entrainment of ThO_2 is insignificant.

After the extensive purging, the reaction chamber and vaporizer section are heated to 1830 F (1270 K). When the desired temperature is attained, 8 to 10 thousand volts are applied to the precipitators and all gas flows are adjusted to the desired levels with the flow through the ThO_2 being adjusted last. The motor drive on the CrI_2 feeder is turned on almost simultaneously with the initiation of flow through the ThO_2. Typical gas gas-flow rates are 5 liters per minute ($8.33 \times 10^{-5} m^3/s$) of helium through the CrI_2 vaporizer, 13 liters per minute ($2.16 \times 10^{-4} m^3/s$) of hydrogen around the quartz plate into the reaction chamber, 1 liter per minute ($1.67 \times 10^{-5} m^3/s$) through the ThO_2 feeder, 5 liters per minute ($8.33 \times 10^{-5} m^3/s$) bypassing the ThO_2, 1 liter per minute ($1.67 \times 10^{-5} m^3/s$) through the housing which contains the small-bore ThO_2 injector tube, and 0.2 liter per minute ($3.34 \times 10^{-6} m^3/s$) through the product flask. The conditions of temperature and flow rate are maintained until either all of the CrI_2 is fed, or the CrI_2-helium nozzle plugs with chromium. The CrI_2 charge ($\approx$480 grams) (0.480 kg) can be fed in about 4 hours' time. To terminate the run, the feed of CrI_2 and ThO_2 is stopped, the flows are reduced to a minimal rate, and power to the heaters and to the precipicator is interrupted. The powder product is pushed from the precipitator into an attached Vycor bulb. Hydrogen at a flow rate of 1 liter per minute ($1.67 \times 10^{-5} m^3/s$) is then passed over the powder product, and the bulb containing the powder is heated at 1470 F (1070 K) for a period of 4 hours to convert residual CrI_2 to chromium. After the reactor is cooled to room temperature, the powder product is transferred to the product flask by tilting the assembly to a near vertical position. The product flask is then sealed by fusion to separate the flask from the preparation unit.